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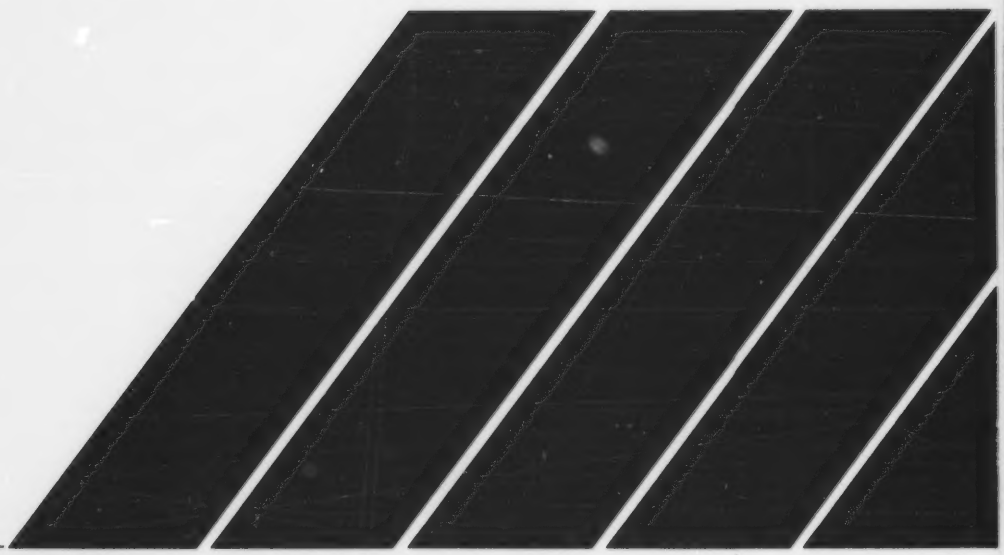
DEVELOPMENT OF A REACTOR FOR THE VACUUM PYROLYSIS OF BIOMASS



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DEVELOPMENT OF A REACTOR FOR THE VACUUM PYROLYSIS OF BIOMASS

PREPARED FOR:

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PREFACE

The present study follows a series of research contracts initiated during 1979. The purpose was to apply and develop the vacuum pyrolysis concept to biomass wood residues. Specific objectives of this study were, (i), to complete the process engineering study in order to enable the technology transfer to the industry; (ii) to perform the process feasibility study; (iii), to investigate at the laboratory scale the upgrading and separation of valuable chemicals which are found in the pyrolysis oil product; (iv) to extend the vacuum pyrolysis process to other types of biomass residues such as Municipal Solid Wastes (MSW).

This research study fits well with the objectives of the Bioenergy Development Program of the Efficiency and Alternative Energy Technology Branch since one of the goals of the Program is to valorize biomass to fuels and chemicals. Vacuum pyrolysis, which is a thermochemical process, represents an original avenue to achieve those objectives. The authors believe that the present study will interest Canadian users who generate biomass residues, recycling equipment, manufacture industries, and the scientific community in general.

ABSTRACT

A continuous vacuum pyrolysis process has been developed to transform biomass into liquid and solid fuels and valuable chemicals. The research program described in this paper is divided in three different sections.

(1) A "Reactor Performance Study" during which 30 kg h^{-1} of wood residues were pyrolysed at 560 °C and a total pressure of 16.7 kPa in a multiple hearth Process Development Unit (PDU). Heat and mass balances as well as heat transfer data for the reactor, the condensers and the vacuum system were generated. The data were then used for the design of a 4 tonnes per hour (4000 kg h^{-1}) capacity pyrolysis plant. An economic analysis showed that the process will be profitable if adequate ugrading of the products and\or collection of a tipping fee for the treatment of wood residues is applied.

(2) Separation of chemicals from the wood residue pyrolysis oils was performed by Liquid Chromatography (LC) on silica gel at the 100 g scale. Six groups of chemicals were segregated among which many valuable chemicals such as vanillin were isolated in concentration above 0.5%. A preliminary feasibility study for a 600 kg h^{-1} wood oil treatment unit showed that purification by LC was not profitable. More advanced techniques such as HPLC and membrane separation techniques should be considered in the future.

(3) Vacuum pyrolysis was applied to Refused Derived Fuel (RDF) prepared from Municipal Solid Waste (MSW). A laboratory batch unit with a 150 g sample was heated to 455 °C and under a total pressure of 1.3 kPa. A mass balance showed that the oil and pitch together represented approximately 35% of the products. GC and GC/MS analyses revealed that the oil contained significant amount (~1%) of maltol and 17% of sugar, mainly glucose. No priority pollutant has been detected in this oil.

RÉSUMÉ

Des chercheurs ont mis au point un procédé de pyrolyse sous vide en continu, en vue de la transformation de la biomasse en combustibles liquides et solides et en produits chimiques de valeur. Le programme de recherche décrit dans le présent rapport comporte trois sections.

1) Dans le cadre d'une «Étude de rendement du réacteur», 30 kg h^{-1} de déchets de bois ont été pyrolysés à une température de 560 °C et sous une pression totale de 16,7 kPa, dans une unité de développement de procédé à soles multiples. L'étude a fourni des données sur les bilans calorifiques et massiques et sur le transfert calorifique pour le réacteur, les condenseurs et le système sous vide. Par la suite, ces données ont servi à la conception d'une usine de pyrolyse d'une capacité de 4 tonnes/heure (4 000 kg h^{-1}). Une analyse économique a révélé que le procédé sera rentable dans la mesure où il y aura enrichissement suffisant des produits ou établissement d'une redevance de déversement pour le traitement des déchets de bois.

2) La séparation des produits chimiques des huiles pyrolytiques dérivées de déchets de bois a été obtenue par chromatographie liquide sur silicagel à l'échelle de 100 g. On a réussi à séparer six groupes de produits chimiques et à isoler de nombreux produits chimiques de valeur, comme la vanilline, à des concentrations supérieures à 0,5 %. Une étude provisoire de la faisabilité d'une unité de traitement de l'huile d'une capacité de 600 kg h^{-1} a montré que la purification par chromatographie liquide n'est pas rentable. À l'avenir, il faudra songer à utiliser d'autres techniques plus perfectionnées, comme la chromatographie liquide à haute performance (CLHP) et la séparation par membrane.

3) Le procédé de pyrolyse sous vide a été utilisé pour des combustibles dérivés de déchets préparés à partir de résidus urbains solides. Un alimenteur-doseur de laboratoire muni d'un échantillon de 150 g a été chauffé à une température de 455 °C, sous une pression totale de 1,3 kPa. Le bilan massique a révélé qu'ensemble, l'huile et le brai constituent environ 35 % des produits. L'analyse par CG et par couplage CG-SM a montré que l'huile contient des quantités significatives (~1 %) de maltol et de sucre (17 %), principalement de glucose. On n'y a décelé aucun polluant principal.

EXECUTIVE SUMMARY

Vacuum pyrolysis is a thermochemical conversion process under development in our laboratories since 1979. The process can be used to recycle and transform biomass residues into valuable chemicals and solid and liquid fuels. The specific objectives of this study were the followings:

- To finalize the performance study on the mechanical configuration and operation for the type of reactor chosen (a pilot plant multiple hearth furnace, 0.7 m in diam. and 2 m high).

- To find the optimum reactor operating conditions for the separation and recovery of different pyrolysis products: oil, charcoal, an aqueous phase and gas.

- To prepare the final design of the contemplated industrial reactor after having obtained the missing data regarding the heat transfer phenomena inside the reactor.

- To achieve a study on the economical feasibility of a 4000 kg h^{-1} biomass vacuum pyrolysis plant based on different market scenarios for the pyrolysis products.

- To investigate the possibility of separating and purifying by Liquid Chromatography the fine chemical compounds found in the pyrolysis oils.

- To generate background data for the pyrolysis at the laboratory scale of Refused Derived Fuels (RDF) materials.

The research program has been organized in three different sections. The most important one is the "Reactor Performance Study" (Chapters 3.0, 4.0, 5.0 and 6.0). The next section is the "Separation of Chemicals from Wood Pyrolysis Oils" (Chapters 7.0, 8.0 and 9.0). The third one is a laboratory study of "RDF vacuum pyrolysis" (Chapter 10.0 of the report). Each section is summarized below.

Reactor performance study

The biomass feedstock used for this series of pyrolysis runs was mainly composed of spruce wood in form of small fibers and chips consisting of 60% wood and 40% bark. The feedstock was provided by BIOSYN from St-Juste-de-Bretenières, P.Q.

The pyrolysis reactor was a six (6) hearth vertical furnace, 2 m height and 0.7 m in diameter. The feedstock was fed at the top and circulated on each plateau towards the bottom, being entrained by a slow-motion raking system. The reactor was electrically heated with elements installed around the reactor cylinder, outside the chamber.

The feed hopper had a capacity of 250 kg. The screw conveyor was carrying the stock from the base of the silo toward the reactor at a specified feeding rate. The conveyor was installed at an angle of 32° with respects to the horizontal and ended in a vertical chute connected to the reactor. Rotating rake system prevented any bridging in the silo and another one in the chute at the end of the screw conveyor breaks biomass conglomerates.

The six-hearth furnace had six ports (38 mm dia.) located at each hearth level for extraction of the pyrolytic vapors and gas produced. Each outlet converged toward a vertical "gas/vapor-collecting manifold" which was itself connected to a first quencher or scrubber, also called the Primary Condensation Unit (PCU), via a flexible metallic union. The purpose of the PCU was to condense the higher molecular weight oil fraction.

A second quencher called the Secondary Condensation Unit (SCU) was used to condense the lighter oils together with most of the steam. It immediatly followed the PCU. The noncondensable pyrolytic gases passed through a tertiary treatment system for condensing the remaining water vapor as well as traces of organic vapors still present in the gases. This ensured the vacuum pump protection as well as clean gas effluent. This tertiary system comprised a tubular condenser with methanol as cooling fluid. The methanol which circulated in a coil passed across a refrigerator where it was cooled to -15°C. The tubular condenser was followed by a cyclone, a dry-ice trap and a filter.

Following this, the non condensable gases circulated across the Edwards E2M-80 vacuum pump, a silica-gel (or an ice) trap and a gas meter, prior to be burned with a gas flare.

The charcoal residue was extracted from the reactor by a screw conveyor installed at its bottom, and was conveyed toward a charcoal bin.

Other modifications were incorporated to the PDU during this study: the rotating arms of the reactor were modified in order to increase the biomass flow rate; a cooling circuit protected the polymer seal of the reactor and allowed to augment the operating temperature; additional thermocouples were installed on the rotating arms and on the inside and outside of the shell in order to collect heat transfer data.

A series of tests was performed in the PDU to evaluate the capability of the pyrolysis unit to handle large feeding rates. Contact time of the solids inside the reactor was set at 30 minutes. Temperature of the last hearth was maintained between 550 and 570°C while temperature of the top hearth was around 250°C. Absolute pressure inside the reactor ranged between 9.3 and 16.7 kPa. The cooling temperature of the PCU and the SCU were set to approximately 40°C and 15°C respectively. During these tests, some technical problems occurred when feeding the PDU at a high flowrate (close to 30 kg h^{-1}): it was sometimes difficult to maintain a stable throughput of wood residues in the reactor over a long period of time.

Results of the proximate analyses of residual charcoals showed that for the same temperature wood conversion was better achieved at lower pressure. 33% wt. volatile material was found in charcoal obtained from pyrolysis at 16.7 kPa while only 19% wt. for the one generated by pyrolysis at 9.3 kPa. Measurements revealed that the power required to maintain vacuum in the system represented only 1/10 of the brake power of the mechanical pump. Measured values for the power required to maintain the temperature of the reactor at the set point and compensate for the heat loss to the ambient were air between 2 900 and 3 600 W. The calculated overall heat transfer coefficient for the heat loss to the ambient air was found between 5.6 and 7.3 $W \cdot m^{-2} \cdot °C^{-1}$. The overall heat transfer coefficient obtained for the quencher of the PCU was between 121 and 142 $W \cdot m^{-2} \cdot °C^{-1}$. Finally the cooling requirement for the charcoal screw-conveyor has been calculated and value between 460 and 470 $KJ \cdot kg^{-1}$ of charcoal were obtained.

Condensation of the pyrolytic vapors with the two quenchers in series, which were operated at 40° and 15° C respectively, was found to be efficient. However, an improved tertiary treatment system should be developed in order to remove traces of water vapor that are still present in the gas stream prior to the vacuum pump.

The experimental results with the PDU were used to prepare a flowsheet for a 4 t/h capacity pyrolysis plant. In this process, the moisture content of 7.9 t/h of the forestry residue is lowered from 50% down to 10% with a rotary dryer. The dryer uses the heat generated by burning a small amount of dry wood flour feedstock. The heat content of the burned flour is equivalent to 1830 kWh. A mill pulverizes the required amount (375 kg $\cdot$ h^{-1}) of dry wood and supplies it to the burner. Some energy is also obtained by combustion of the pyrolytic gases (690 kWh) in the gas burner. Four tons per hour (4 t/h) of wood chips (10% moisture) are fed with an airtight screw feeder in a battery of three multiple hearth furnaces in parallel (1.3 t/h capacity each). A total energy of 1300 kWh (25% heat loss has been accounted) is required to heat the three electrical pyrolysis furnaces. During pyrolysis, organic vapors, steam and non condensable gases are formed.

Two quenching towers in series condense the organic vapors and steam. Temperature of the first and second quenchers was adjusted so that the heavier oil phase collected at the Primary Condensing Unit contained almost no water (3% moisture). This oil phase production rate is 1 415 kg $\cdot$ h^{-1}. Most of the water as well as the light oil phase were condensed in the secondary condensing unit. The two liquids recovered at this secondary stage are miscible and constitute an homogeneous aqueous phase which amounts for 1 415 kg $\cdot$ h^{-1} with a 2:1, water to light oil ratio. No special water treatment unit was included during the design since the aqueous phase would be disposed of by burning it at the dryer stage. The calorific value of the light oil present in the aqueous phase is recovered to evaporate the water contained in the aqueous phase.

The non condensable gas (360 kg $\cdot$ h^{-1}) is removed by the vacuum pump and is expelled at a pressure slightly higher than atmospheric pressure towards the burner for the wood dryer. The charcoal (960 kg $\cdot$ h^{-1} anhydrous) is collected at the bottom of the three reactors using screw devices externally cooled with tap water. Then water is sprayed over the charcoal in a transfer bin to help cooling it. The resulting slurry is removed from the vacuum system by a slurry pump.

Finally the water is removed from the slurry by centrifugation leaving 2 880 kg · h^{-1} of moistened solid charcoal (66.7% moisture) which can be used as a fuel or as a metallugical coke when dried.

A profitability study was done based on three different scenarios for a 4 t/h capacity plant. The fixed capital investment for this plant was estimated to be $ CAN 12 M. It was assumed that the heavy oil product would be sold at $20/bbl. Wood charcoal used as a solid fuel is worth 30/t; used as metallurgical coke, $75/t. The price of charcoal upgraded to activated carbon was estimated to be not less than $1000/t. It was assumed however that the activation process would yield only 30% of activated carbon from the initial charcoal feedstock. The three (3) previous scenarios were re-evaluated after a tipping fee of $30/t of wood waste treated was included as an income.

The study showed that without collecting a tipping fee, the process generates annual profits only when the charcoal is upgraded to activated carbon ($ CAN 0,4 M). The collection of a $30/t tipping fee makes the process much more attractive since it represents $ CAN 1.7 M income increase per year. So the total before tax profits become $2.1 M if the charcoal is sold as activated carbon $0.4 M if as coke and $0.06 M if as fuel.

Separation of chemicals from wood pyrolysis oils

The purpose of this part of the study was to investigate the potential for the separation by liquid chromatography at the laboratory scale of the many chemical compounds which are found in wood pyrolysis oils. For that purporse a preparative LC system was used to process relatively large quantities of oil (100 g) and then evaluate the feasibility of an industrial unit (600 kg/day).

A transparent double jacket tube was used to build the preparative LC column. The inside tube was made of a glass column 1250 mm X 75 mm i.d. and 5 mm thick; the outside jacket was made of amount of silica gel needed was approximately 20 to 30 times by weight of the amount sample to be separated. The height to diameter ratio for the packed bed was approximately 10:1.

In the preparative LC column separation , the solvent sequence illustrated in the table that follows

was used depending on the preliminary result of the analytical separation. Six groups were collected according to their functionalities and were subsequently vacuum distilled. The separated fractions were analyzed by GC and GC/MS.

Further purification of the rare chemicals present in the subfractions, which were collected during the preparative LC separation was accomplished by thin layer chromatography.

Liquid Chromatography Elution Sequence

Group No.	Eluent
1	10% CH_2Cl_2 in petroleum ether
2	40% CH_2Cl_2 in petroleum ether
3	70% CH_2Cl_2 in petroleum ether
4	100% CH_2Cl_2
5	100% Ethyl acetate
6	10% Formic acid in methanol

Chemical analysis revealed that the composition of the 6 groups were as follows:

Group 1 was mainly composed of straight-chain hydrocarbons, dominated with alkanes and alkenes ranging from C_{14} to C_{28} carbon numbers. In addition , some branched chain saturated hydrocarbons and some substituted aromatic compounds were identified in this group.

Group 2 contained many aromatic type compounds of the alkyl benzene series but a few phenolic compounds were also found in this group.

Six major peaks which were mainly composed of phenolic compounds were observed in group 3.

Group 4 was composed of polar oxygenated compounds such as aldehydes, cycloketones and highly complex ester compounds.

Group 5 was similar to group 4. The major peaks represented oxygenated compounds. It was mainly composed of cycloketones and vanillin. The most interesting discovery of Group 5 was the detection of 2-methylcyclopenten-1-one and 2 (3H)-furanon; their respective concentration exceeded 0.5% by wt on an anhydrous and acid-free oil basis. In this group only vanillin (4-hydroxy-3-methoxybenzaldehyde) was found in concentration above 1 %.

Group 6 was composed of strongly polar compounds such as sugar and polymers, which showed no significant response on GS/MS . However the yield for this group reached 44% by weight on an anhydrous and acid - free oil basis. This indicated that most compounds present in wood pyrolysis oils were highly polar and non volatile compounds. These compounds probably could be further transformed into different detectable compounds, for example by hydrolysis.

A mass balance for the preparative liquid chromatography separation of 100 g (as-received basis) over 2 kg silica gel produced various chemicals including 1.5 g hydrocarbons, 6.7 g aromatic compounds, 6.7 g phenols, 27.3 g oxygenated compounds and 32.5 g polymeric compounds. The separation requested approximately 36 kg of solvents. More than 96 % of the eluting solvents was recovered by vacuum distillation . The spent silica gel was regenerated and reused. 4 % of silica gel was lost during the regeneration process.

The effect of the silica gel moisture content on the preparative LC separation was studied in the range of 3.2% to 13.1% (by weight). It was found that the composition of the individual fractions was strongly affected by the silica gel water content. However when the same operation conditions were repeated the chromatographic separation was reproducible with less than 5% discrepancy.

The regeneration of silica gel was achieved at high temperature (400-600°C) in a furnace. The regenerated silica gel showed only slightly less activity than the fresh silica gel, due to the chemical alteration by highly polar solvents, such as formic acid.

A preliminary economical study was undertaken to estimate the feasibility of the LC separation process applied to a 600 kg $\cdot$ h^{-1} wood pyrolysis oil plant. The study which accounted for the cost of recycling or regenarating the stationnary phase and the eluents, revealed that more than

50% of the costs come from solvent and silica gel losses.

Selling the products as gross hydrocarbons, phenolics, etc... is not attractive. More intensive separation must be done in order to extract pure substances with improved market values. Improvements will be required to reach profitability. Better solvent recovery and better silica-gel regeneration, or the use of more efficient separation techniques than LC (such as HPLC or membrane technology) should be investigated to obtain a better performance and lower operation costs.

Vacuum pyrolysis of Refused Derived Fuels (RDF)

Refused Derived Fuels (RDF) were prepared from Municipal Solid Waste MSW produced at Ville de Laval, P. Qué. The RDF briquettes were compressed at a temperature of 170°C. The outlet temperature was 110°C. The briquettes were broken in smaller pieces (1/8" -1/2") and were predried at 80°C prior to pyrolysis. The proximate analysis of the initial feedstock gave 59.8% volatile matters, 29.1% ash and 11.1% fixed carbon. The sample moisture content was 3.1%.

The vacuum pyrolysis experiments were performed in a 1 liter batch reactor with approximately 150 g of RDF at a maximum temperature of 455°C and an average total pressure of 1.3 kPa. The pyrolysis oils were recovered in a series of three cooling traps at 0°C, -78°C and -78°C, respectively.

In this work we also report a fractionation scheme and partial analysis of the oil fractions. The analyses were made by means of gas-chromatography (GC) and gas-chromatography coupled to a mass spectrometer (GC/MS).

Pyrolysis of the RDF sample produced 44.4% residual solids, 35.1% oils + pitch, 8.1% gas, 9.3% pyrolysis water and 3.1% moisture (wt. %, feedstock as-received basis). On an organic basis, the yields were 23.5% solids, 51.1% oils + pitch, 11.8% pyrolytic water and 13.6% gas. The mass balance closed to 99.7%.

The proximate analysis of the solid residues gave 11.6% volatile matters, 62.0% ash and 26.4% fixed carbon. The hygroscopic moisture in the sample was 1.4%.

Pyrolysis oil was mainly oxygenated in nature and has presumably a low molecular weight distribution range. Significant quantity of maltol (~ 1%) which is a food aroma was positively identified. In addition we found about 17% sugar, mainly glucose. Complete toxicity measurement of the oil has not been made. However we have not identified at this point any priority pollutants including chlorinated nor nonchlorinated volatile hydrocarbons, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in the oil phase. Only trace amounts of chlorinated volatiles were observed in the gas phase. The oil has a low concentration of phenolic compounds which could be easily separated if required.

Pyrolysis pitch is particularly attractive since it can be fractionated into interesting classes of compounds such as aliphatic hydrocarbons, benzene derivatives, carboxylic acid esters, phenolic compounds and phthalate esters. These contributed for about 70-80% of the total pitch. Aliphatic hydrocarbons can be used as wax, phthalate esters can be recycled in the polymer industry as plasticizers and carboxylic esters can be recycled in the detergent manufacture.

Conclusions

The PDU was operated during sufficient lengths of time to establish good mass and energy balances. Condensation with quenchers at the primary and secondary condensing units (PCU and SCU) proved successful. It seems possible to adjust the operation conditions, such as the temperature of the PCU and the internal pressure of the system, in order to obtain oil with a low water content. Some problems were encountered with the solid feeding system of the multiple hearth reactor. However we consider these are minor difficulties that could be easily solved with an improved mechanical design.

The heat requirement for the pyrolysis of wood residue is around 400 $kJ \cdot kg^{-1}$ (wood feedstock basis). Also in our relatively small scale PDU, heat losses to the atmosphere are quite important since they represent roughly 1/3 to 1/2 of the total electric power required by the reactor. The heat transfer coefficient for the outer shell of the reactor with the ambient atmosphere was

estimated to range between 5.6 and 7.3 $W \cdot m^{-2} \cdot C^{-1}$. Also the ratio of the effective pumping power for the pyrolytic vapors and gas over the total pumping power is in the 10% range. The heat transfer coefficients mesured in the quencher at the PCU ranged between 121 and 142 $W \cdot m^{-2} \cdot C^{-1}$. The heat required for cooling the charcoal product stream was around 465 $kJ \cdot kg^{-1}$ of charcoal.

A preliminary evaluation of the technical feasibility of a 4 t/h plant for the treatment of wood chips under certain conditions was done. The study supposed drying the wood chips to 10% humidity content prior to the pyrolysis step. The process is economically attractive if the charcoal product is activated to an active carbon. However the inclusion of a tipping fee of $30/tonne makes the process much more attractive.

Separation of the chemicals from the oil was performed in a reproductive way using Liquid Chromatography (LC) technique at the 100 g scale. Valuable fine chemicals such as vanillin were identified and separated. However more work has to be done to improve the LC technique used in order to render the extraction and purification of fine chemicals an economical step.

Finally laboratory scale pyrolysis tests were performed on MSW. Many chemicals such as maltol and glucose were identified in the oil and pitch fractions. No priority pollutants such as chlorinated and non chlorinated volatile hydrocarbons, polycyclic aromatics and polychlorinated biphenyls have been identified in the oil.

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1.0 INTRODUCTION

The vacuum pyrolysis process is under development in our laboratories since 1979. Our goals were the followings:

- To establish at the laboratory scale the yields and the general characteristics of products obtained on vacuum pyrolysis of wood.

- To test the vacuum pyrolysis concept using a Process Development Unit (P.D.U.) centred around a multiple hearth furnace.

- To determine the optimal operating conditions of the P.D.U. to get the maximum yield of oils, separated from the aqueous phase.

- To conduct a preliminary investigation of the performance of the type of reactor selected at moderate feeding rate.

Work performed till 1988 is summarized in DSS contract report # 23283-7-6334/01-SZ "Performance Study of a Process Development Unit for the Vacuum Pyrolysis of Biomass", submitted to the Renewable Energies Division/Energy Mines and Ressources Canada (1). This study concluded that the vacuum pyrolysis process represented a valid and promising approach for the transformation of forestry wastes to fuels and high-value fine chemicals. Moreover, a preliminary economic study concluded that the process would be more profitable if the separation and recovery of the fine chemicals contained in the liquid phases were recovered during the pyrolysis process.

The present study covers the work performed along the same line during the period comprised between August 1988 and March 1990. The main objective of this work was to continue the process engineering study in order to transfer the technology to the industry.

2.0 SPECIFIC OBJECTIVES

The research program performed on vacuum pyrolysis in the past used a 0.7 m in diameter by 2 m height vertical reactor composed of six (6) hearths which i) enabled to identify the optimum operating conditions to obtain high yields of oils, ii) to obtain engineering data on the heat transfer modes in the reactor, iii) to determine the heat required for pyrolysis, iv) to determine the capacity of the reactor prototype, and v), to get economical data about the feasibility of a commercial plant.

However, some aspects of the R & D studies were not covered in the past, like the mechanical and the thermal problems associated with a multiple hearth reactor.

The specific objectives of this work were:

- To complete the performance study on the mechanical configuration and operation for the type of reactor chosen (multiple hearth furnace).

- To identify the optimum operating conditions of the reactor which permit to separate and recover the different pyrolysis products: oils, charcoal, aqueous phase and gas.

- To prepare the final design for the contemplated industrial reactor after obtaining the missing data on the heat transfer phenomena inside the reactor.

- To complete the study on the economical feasibility of a 4000 kg h^{-1} biomass vacuum pyrolysis plant based on different market scenarios for the pyrolysis products.

- To investigate the possibility of separating and purifying fine chemicals found in the pyrolysis oils.

- To get background data for the pyrolysis at the laboratory scale of Refused Derived Fuels (RDF).

3.0 REACTOR PERFORMANCE STUDY

In this section, we make a general description of the Process Development Unit (P.D.U.), and a description of each component of the system, including all modifications that were necessary.

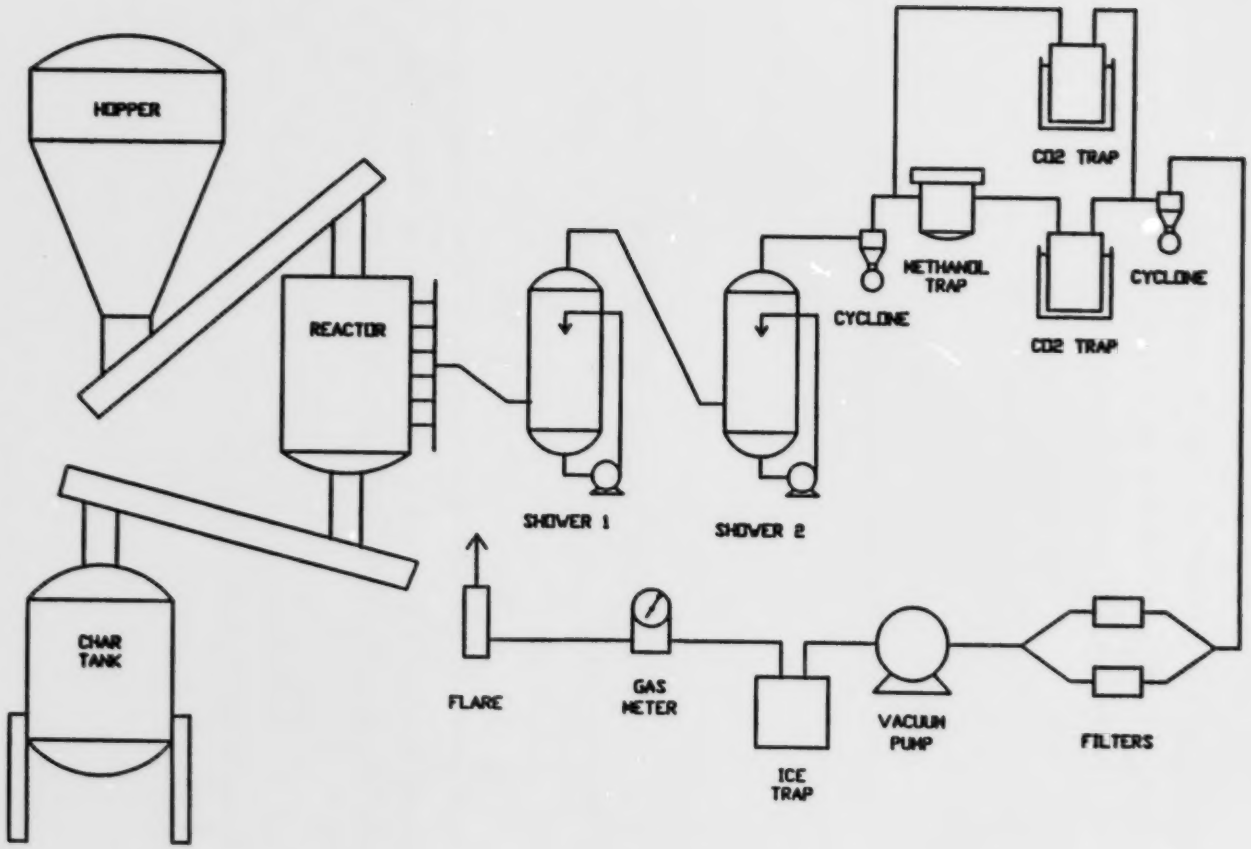
3.1 General Description of the P.D.U.

Figure 1 represents a flow sheet of the Process Development Unit used during the experimentation.

The pyrolysis reactor is a six (6) hearth vertical furnace, 2 m height and 0.7 m in diameter. The feedstock was fed at the top and circulated on each plateau towards the bottom, being entrained by a slow-motion raking system. The reactor was electrically heated with elements installed around the reactor cylinder, outside the chamber.

The biomass feedstock was mainly composed of spruce wood in form of small fibers and chips consisting of 60% wood and 40% bark and was provided by BIOSYN from St-Juste-de-Bretenières, P.Q..

FIGURE 1: General Schematic of the Process Development Unit (PDU)



The feed hopper had a capacity of 250 kg. The screw conveyor, 150 mm in diameter by 2.7 m long, was driven by a DC motor-reducer (250:1) unit and was carrying the stock from the base of the silo toward the reactor at a specified feeding rate. The conveyor was installed at an angle of 32° with respects to the horizontal and ended in a vertical chute connected to the reactor.

The six-hearth furnace had six ports (38 mm dia.) located at each hearth level for extraction of the pyrolytic vapors and gas produced. Each outlet converged toward a vertical "gas/vapor-collecting manifold" which was itself connected to a first quencher or scrubber, also called the Primary Condensation Unit (PCU), via a flexible metallic union. The purpose of the PCU was to condense the higher molecular weight oil fraction.

A second quencher called the Secondary Condensation Unit (SCU) was used to condense the lighter oils together with most of the steam. It immediatly followed the PCU. The noncondensable pyrolytic gases passed through a tertiary treatment system for condensing the remaining water vapor as well as traces of organic vapors still present in the gases. This ensured the vacuum pump protection as well as clean gas effluent. This tertiary system comprised a tubular condenser with methanol as cooling fluid. The methanol which circulated in a coil passed across a refrigerator where it was cooled to -15°C. The tubular condenser was followed by a cyclone, a dry-ice trap and a filter (see Figure 1).

Following this, the non condensable gases circulated across the Edwards E2M-80 vacuum pump, a silica-gel (or an ice) trap and a gas meter, prior to be burned with a gas torch.

The charcoal residue was extracted from the reactor by a screw conveyor installed at its bottom, and was conveyed toward a charcoal bin.

The runs were conducted at an absolute pressure of 9.3 to 16.7 kPa and pyrolysis temperatures of 550-570°C at the bottom of the reactor. The cooling temperatures of the PCU and the SCU units were approximately 40°C and 15°C, respectively.

3.2 Description of the P.D.U. Component Units

3.2.1 Reactor

The main goal was to operate the reactor at the highest possible flow rate. The reader shall read reference 1 to obtain a description of the original reactor that has been modified during the present mandate.

First of all, the design of the rotating arms of the reactor was modified to increase the flow rate.

A cooling circuit was installed near the sealing gasket of the cover, in order to protect the Viton gasket for the runs performed during this contract at higher pyrolysis temperatures compared to previous the experiments (550°C - 570°C vs 500°C).

The six shell and tube heat exchangers previously installed for the product outlets were dismantled and substituted with heat traced connecting pipes. The vertical manifold connected to the six vapors exit conducts was made of copper initially. It was rebuilt in stainless steel after it was damaged just before run D011.

The heating power (44 kW) of the reactor was provided by electric elements installed on the outer surface of the shell.

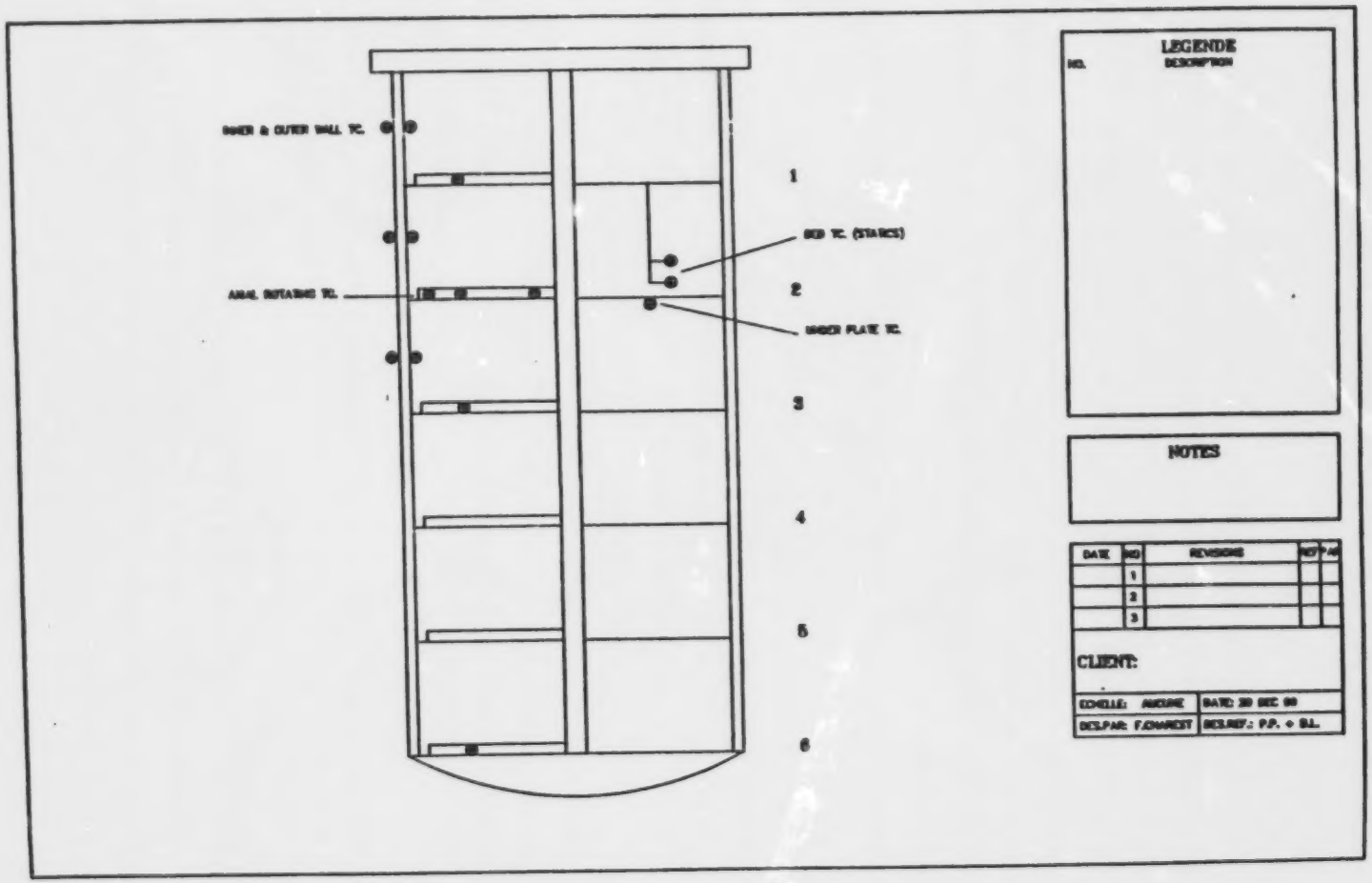
Additional thermocouples were installed on top of the rotating arms of the carrier system at the 1st, 2nd and 3rd hearth levels. The objective was to monitor the temperature variations as a function of the hearth level and as a function also of the position with respects to the

heating wall. Hence, a thermocouple was installed on one arm for hearth # 1 and # 3, and three thermocouples were installed along one carrier arm at the hearth # 2 level, as shown in Figure 2.

Six more thermocouples were also installed on the inside wall of the reactor at the 1st, 2nd and 3rd hearth levels, opposite to some of the thermocouples located on the external side of the wall between the electric elements. Two more thermocouples were also installed at the 2nd hearth level to record the biomass bed temperature as shown in Figure 2.

Finally, in order to calculate the heat transfer coefficient from the reactor to the surroundings, eight thermocouples were installed outside the reactor, near the surface of the insulating material covering the reactor.

FIGURE 2: Thermocouple Positions for Heat Transfer Calculations



3.2.2 Feeding System

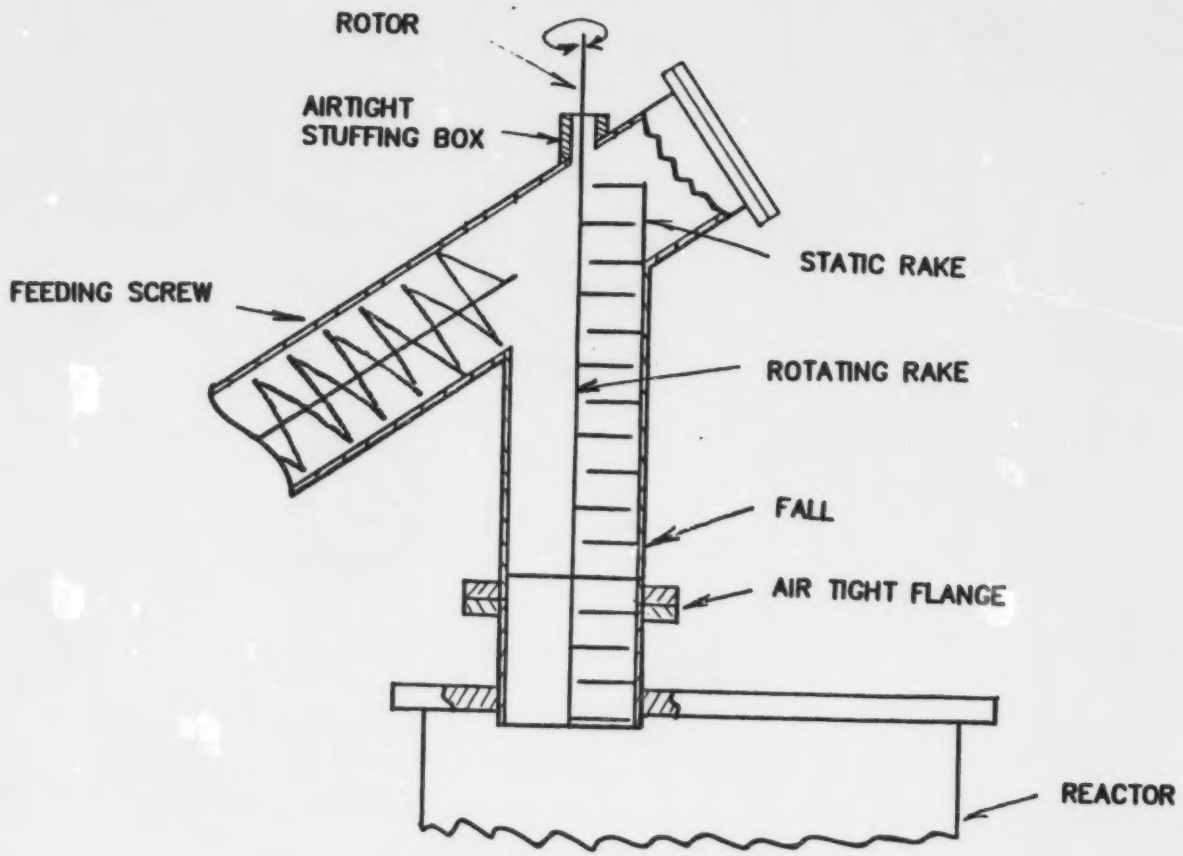
The feeding system of the P.D.U. was composed of a 250 kg capacity silo, and a screw conveyor connecting the silo and the reactor via a rubber flange.

A shaking device made of metallic rods was installed inside the silo to break and prevent any bridging of the feedstock material and insure a regular outflow down the conveyor. This shaking system was pneumatically actuated.

The conveyor used an Archimede screw driven by a 1/3 HP DC motor-reducer (250:1) system.

In order to prevent the blocking of biomass material in the vertical chute near the reactor head, it was necessary to install a system to break down the feedstock material which formed conglomerates in the chute. This system was made of fixed and rotating rakes which intercrossed (see Figure 3).

FIGURE 3: Feeder Chute Rakes System

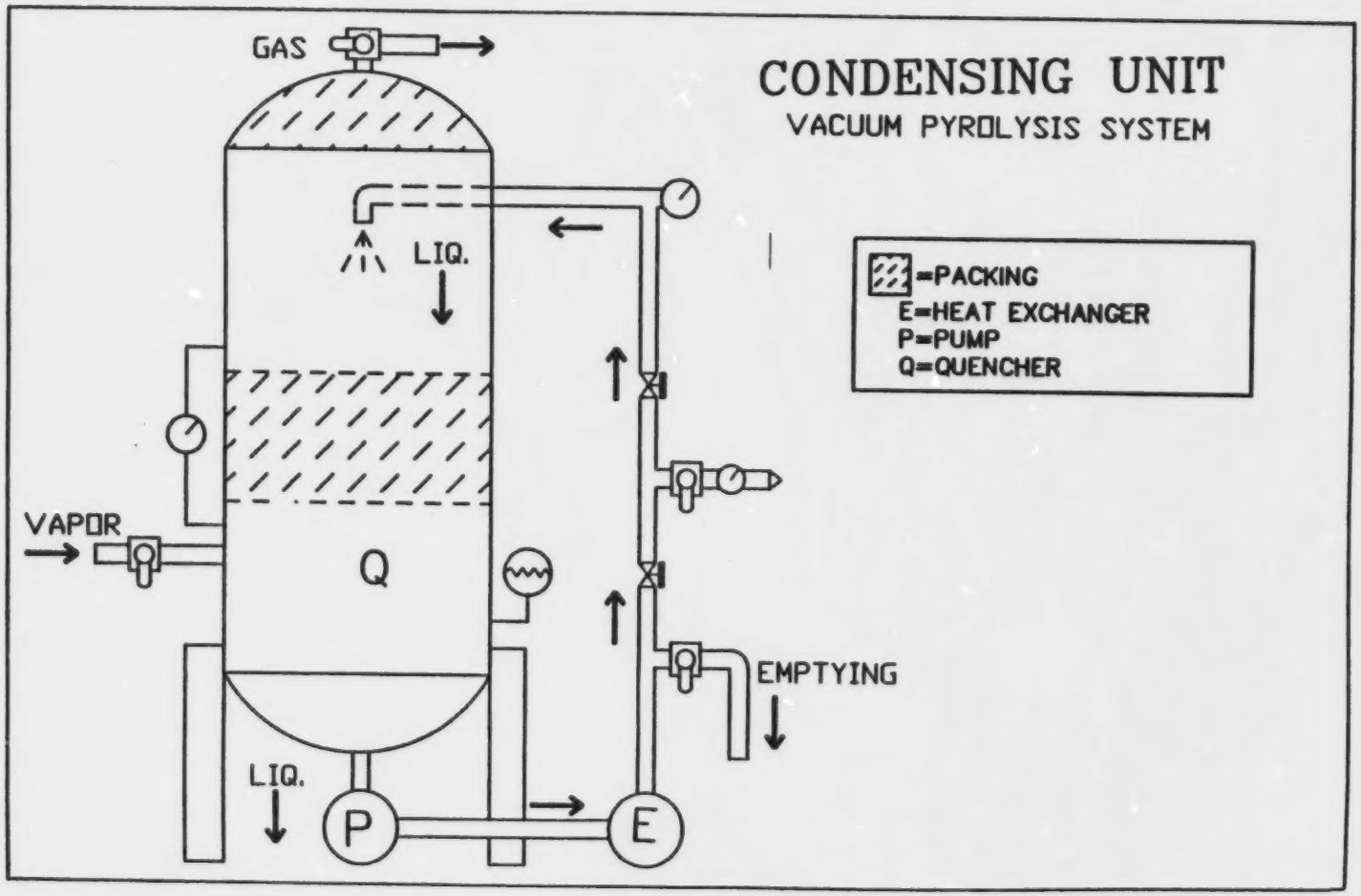


3.2.3 Primary Condensing Unit (PCU)

A drawing of the PCU (1st quencher) is shown in Figure 4. This quencher was used to condense most of the high molecular weight oils and in a lesser proportion the lighter oils and most of the water. It was made of stainless steel.

Vapors coming from the main manifold entered the lower part of the quencher and passed across a 300 mm thick packed bed (25 mm dia. Rashig rings) for heat exchange. The condensates percolated after being showered at the top of the quencher. The condensates were recirculated at a high flow rate with a 0.4 L $\cdot s^{-1}$ pump (or 1400 kg $\cdot h^{-1}$) capacity, while the flow rate of vapors entering the quencher was of the order of 15 kg $\cdot h^{-1}$. Centrifugal and gear-type pumps have been tested for the fluid recirculation. A 5.9 m^2 heat exchanger using tap water was used to cool down the recirculated liquid and to control the gas outlet temperature of the quencher.

FIGURE 4: Primary Condensing Unit (PCU)



A float installed at the lower portion of the quencher actuated a solenoid valve at the pump exit to drive a fraction of the condensed liquids in an accumulation tank, when the liquids level reached a specified level in the quencher.

Temperature of the condensed products leaving the quencher was around 40-50°C, while the inlet temperature of the inlet gas/vapor stream was typically 300°C.

3.2.4 Secondary Condensing Unit (SCU)

After the PCU, the remaining vapor and non condensed gases mixture has moved toward a 2nd quencher, also call the Secondary Condensation Unit (SCU), via a flexible plastic tube of 38 mm in diameter. The design of this quencher was identical to the first one, except it was made of carbon steel instead of stainless steel.

In this quencher most of the light oil vapor fraction was condensed together with the pyrolytic water and moisture vapor. The cooling fluid of the heat exchanger for this unit was water which was chilled to 0°C with ice, by means of a recirculation loop or coil.

The gas/vapor temperature at the quencher exit was approximately 10-15°C.

3.2.5 Gas Treatment System

The gas treatment system also called the Tertiary Condensation Unit (TCU), comprised a cyclone, a tubular heat condenser, a dry-ice trap and a filter preceeding the vacuum pump (see Figure 1).

Methanol was used as cooling fluid used in the tubular condenser. It was cooled down to -15°C with a refrigeration unit in the recirculation loop. After the methanol condenser, the gaseous stream flowed in a second trap kept in an acetone bath and maintained at -80°C, by addition of dry ice. Two filters were installed in parallel after the dry ice trap. Each simply consisted of a standard automobile oil filter.

During this contract work, both silica-gel (Adrelite/$CaSO_4$) and ice traps were tested to condense water and moisture vapor still contained in the gaseous stream following the vacuum pump, before it could reach the gas meter.

3.2.6 Gas Meter

A gas meter at the exit of the vacuum pump recorded the volumetric flow of uncondensable gases produced during pyrolysis.

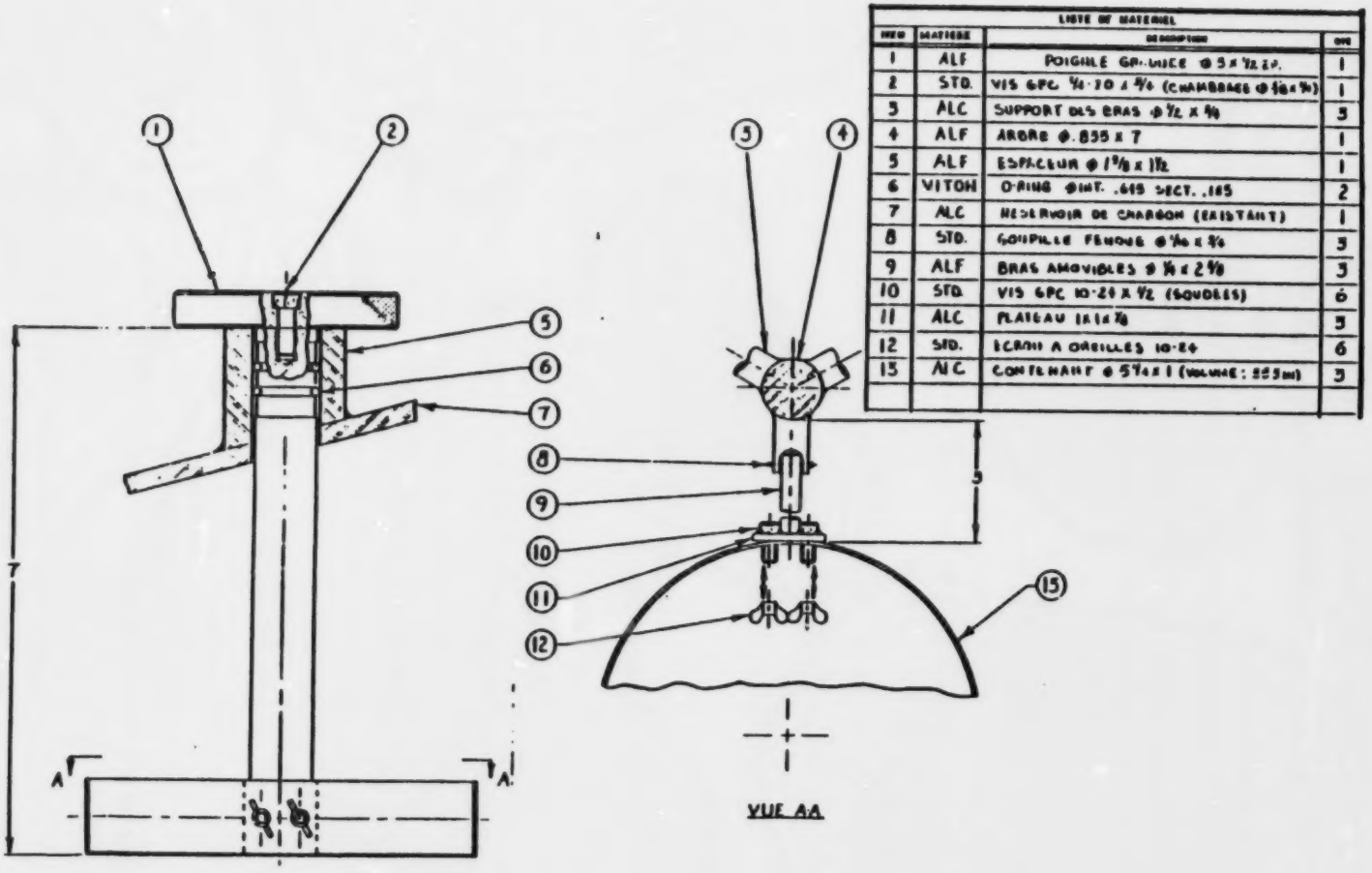
3.2.7 Gas Torch

The gaseous stream from the gas meter was burned in a gas torch. In a commercial plant this gas could be used for drying the biomass inlet material.

3.2.8 Charcoal Extraction System

The charcoal residue was extracted from the reactor by a screw conveyor which carried the material to a bin. A copper gasket insured the airtightness of the seal between the flanges of the reactor exit port and the conveyer. The conveyor was equipped with a double wall for cooling purposes with water. Thermocouples were installed at the inlet and outlet ports of the cooling water for heat transfer calculations.

FIGURE 5: Charcoal Sampling System



LISTE DE MATERIEL

REP	MATIERE	DESCRIPTION	QTE
1	ALF	POIGNEE GRAVUREE Ø 5 x 1/2 LG.	1
2	STD.	VIS 6PC 1/4-20 x 3/4 (CHAMBRAGE Ø 5/8 x 3/4)	1
3	ALC	SUPPORT DES BRAS Ø 1/2 x 3/4	3
4	ALF	ARBRE Ø .835 x 7	1
5	ALF	ESPACEUR Ø 1 3/8 x 1 1/2	1
6	VITON	O-RING Ø INT. .615 SECT. .103	2
7	ALC	RESERVOIR DE CHARBON (EXISTANT)	1
8	STD.	GOUPILLE FENDUE Ø 1/16 x 3/4	3
9	ALF	BRAS AMOVIBLES Ø 1/8 x 2 3/8	3
10	STD.	VIS 6PC 10-24 x 1/2 (SOUDEES)	6
11	ALC	PLATEAU 1x1x 3/8	3
12	STD.	ECROU A OREILLES 10-24	6
13	ALC	CONTENANT Ø 5 1/4 x 1 (VOLUME : 555 ml)	3

3.2.9 Charcoal Bin

The charcoal bin had a capacity of 0.6 m^3. A sampling system installed inside the tank enabled to collect three samples of charcoal falling in the tank during one experiment (see Figure 5). A water spray system was also installed in the tank with which cooling water could be showered over the hot charcoal to quench it at regular intervals.

4.0 RESULTS

The multiple hearth reactor prototype was tested to get the following engineering information:

- The global electric power consumed for heating the reactor as a function of the pyrolysis temperature;
- The electric power consumed by the vacuum pump as a function of the pyrolysis temperature;
- The heat transferred from the reactor to the atmosphere and the convective heat transfer coefficient to the surrounding as a function of the pyrolysis temperature;
- The quantity of heat exchanged in the PCU, and the associated heat transfer coefficient for the unit;
- The quantity of heat transferred at the charcoal conveyor level;

The data obtained with the P.D.U., enabled us to estimate the total energy balance around the reactor which was then used to determine the overall energy balance for the process.

Another task undertaken was to calculate, based on the engineering data obtained, the size of an industrial with a capacity of 4000 kg h^{-1}.

In what follows, we provided a summary of the main results obtained during three runs (D011, D012 and D013) that were performed with the P.D.U. during this mandate. We are also reporting on particular problems encountered and on actions taken to solve them.

Experimental data regarding the electric power consumed after heating the reactor and operating the vacuum pump are also presented, as well as calculation results concerning the amount of heat transferred in the various PDU component units, and the associated heat transfer coefficients.

4.1 Runs D011, D012 and D013

Runs D011, D012 and D013 were performed between February 1989 and May 1989. The proximate and elemental analyses of the feedstock material, as well as its calorific value, are presented in Table 1:

TABLE 1: Chemical Characterization of the Feedstock Used for Runs D010 to D012

1. Moisture (as received basis)	6.7%
2. Proximate analysis (dry basis)	
Ash	1.99%
Volatile matter	79.11%
Fixed carbon	18.90%
3. Elemental analysis (organic basis)	
Carbon	44.90%
Hydrogen	6.10%
Nitrogen	0.09%
Sulfur (total)	0.10%
Oxygen (by difference)	48.81%
4. Calorific Value	5000 cal g^{-1}

4.1.1 Run D011

This run lasted three (3) hours. It was stopped when blocking of the feed system occurred due to the wood fiber feedstock material itself. The reactor mean pyrolysis temperature was then 550°C under an absolute pressure of 10.7 kPa. The feedstock flow rate was set at 25 kg · h^{-1} for the first 90 min, and was increased to 40 kg h^{-1}. Blocking of the fibers occurred some time after, near the vertical chute zone at the end of the screw conveyor. A raking system to dismember the fibers conglomerates, as shown in Figure 3, was installed in the chute for the subsequent runs, and proved to be effective.

Another problem was the presence of 2 L of condensed liquids found at the extracting screw level after the run. Also, an accumulation of charcoal was detected between the reactor bottom exit port up and the lowest hearth level. The charcoal conveyor was tested for watertightness from its water jacket and proved to be correct. It was concluded that some vapors had condensed near the bellow level connecting the charcoal conveyor and the charcoal exit port of the reactor, which was not enough insulated so that the charcoal after getting wet was bridging at the exit port. It was decided to insulate the bellow for the next run in order to keep it warmer and prevent any further oil condensation.

The 0.72 m^2 heat exchanger of the 1st quencher revealed to be just large enough to cool down the condensates close to the set point (40°C) fixed for the quencher. For that reason a high flow rate of cooling water had to be used. However some pyrolytic water was found in both the vacuum pump and in the gas meter. It was then decided to use a silica gel trap prior to the gas meter for the next run.

It was also decided to replace the thermocouples at the entry and exit ports of the heat exchangers of the charcoal screw conveyer and the 1st quencher by using differential thermocouples for better precision. Only ungrounded thermocouples were used everywhere in the system.

4.1.2 Run D012

Run D012 lasted four (4) hours. The objective was to operate at a feedrate of 35 kg · h^{-1}. The observed mean flowrate appeared to be only 28 kg · h^{-1}, due to another bridging problem which occurred at intervals inside the silo. The reactor pyrolysis temperature was then 560°C under an absolute pressure of about 9.3 kPa.

The run was stopped after the 1st quencher temperature went out of control because the recirculation pump for this unit progressively lost its pumping capacity under the prevailing vacuum. As a result of excessive temperature inside the 1st quencher, the gas outlet temperature gradually increased and the flexible plastic gut connecting the 1st and 2nd quencher softened and flattened due to the combined effect of heat and vacuum.

It was decided for the next run to replace the centrifugal pump by a gear-type pump of larger capacity, and to substitute the 0.7 m^2 heat exchanger by a larger one (5.9 m^2). The raking system inside the silo was also modified in order to prevent bridging.

The silica-gel trap (Adrelite/$CaSO_4$) was insufficient to condense the water vapor still contained in the gas after the pump. A certain amount of water was still found in the gas meter at the end of the test. For the next run, it was decided to replace the silica-gel trap by a larger 3 L ice trap.

4.1.3 Run D013

This run lasted five (5) hours. The feeding rate was set at 35 kg · h^{-1}. However due to some difficulties with the feeding system, an effective flow rate of 27 kg · h^{-1} only was reached. The pyrolysis temperature was 570°C and the vacuum pressure 16.7 kPa.

The run was stopped when the biomass screw conveyer blocked. This was caused by metallic pieces of the raking system in the silo which broke and fell apart. Some pieces fell down into the conveyer, then blocking the screw and damaging it; even some metallic parts were found in the charcoal reservoir after the test.

During this run the heat exchanger of the 1st quencher unit was found very effective. However the gear-pump tested lost much of its pumping capacity when the vacuum pressure fluctuated under 13.3 kPa. We believe this was caused by some cavitation phenomena.

Traces of water were still found in the vacuum pump and the gas meter.

4.2 Thermal Aspects

4.2.1 Reactor Heating

The global electric powers consumed for heating the reactor during runs D011, D012 and D013 were measured and are presented in Table 2.

TABLE 2: Experimental Conditions and Reactor Power Consumption for Runs D011, D012 and D013

Run	Average Feeding Rate $kg \cdot h^{-1}$	Pyrolysis Temperature °C	Absolute Pressure kPa	Electric Power W	Heat Loss W	Heat of Pyrolysis W
D011	30	550	10.7	6878	3534	3344
D012	28	560	9.3	6450	2915	3535
D013	27	570	16.7	8915	3639	5272

For run D012 the energy required for heating the reactor at the specified temperature and to offset the calorific losses was 2915 W, while it was 3534 W and 3639 W for runs D011 and D013 respectively. The average pyrolysis heats for runs D011, D012 and D013 have been estimated at 3344 W, 3535 W and 5276 W respectively.

It would be also interesting to report the heat requirement on a feedstock weight unit basis. For runs D011, D012 and D013 the calculated values are respectively 400, 455 and 700 kJ kg^{-1} of the as received wood (6.7% moisture). The difficulty to maintain a stable rate due to the high troughput imposed during these three tests is probably the main cause of variation in

our calculations. However the values for runs D011 and D012 fit relatively well with the previously reported value of 350 kJ kg^{-1} (1) where pyrolysis was conducted at a lower rate. We believe that run D013 in particular gave a higher value mainly because of experimental problems which caused unsteady conditions for the thermal balance. One has to keep in mind that the main objective of these three tests was to evaluate the mechanical aspects of the PDU under severe operating conditions. The thermal aspects of the PDU have been already covered in reference 1 under more appropriate operating conditions.

4.2.2 Pumping Power

The Edwards model E2M80, vacuum pump operated with a 600-V, 3 phase voltage.

The electric power consumed by the pump was calculated with the formula:

$$P_{pump} = V I 3^{1/2}$$

where I is the current and V the voltage.

The total pumping power recorded during these runs and the additional power required to remove the pyrolytic vapors and gas, with respects to the consumed power prior to feeding the reactor with biomass, was the following:

TABLE 3: Pumping Power for Runs D011, D012 and D013

Run	Total Pressure (kPa)	Total Pumping Power, P_t W	Additional Power Required for Pyrolytic Vapor/Gas, P_p W	Ratio P_p/P_t
D011	10.7	4082	314	0.08
D012	9.3	4675	430	0.09
D013	16.7	4140	451	0.11

The ratio of the effective pumping power for the pyrolytic vapors and gas over the total pumping power is approximately 10%.

4.2.3 Heat Exchange Around Quencher # 1

The quantity of heat transferred in the quencher # 1 (PCU) heat exchanger was determined for runs D012 and D013. In a condensing unit, the heat recovered from the hot vapor at the quencher level is removed by a cooling water circulation in a shell and tube heat exchanger (Figure 4, item E). If we assume that the heat loss is negligible, it is possible to evaluate the amount of heat released by the condensation of the vapor simply by a mass and energy balance around the heat exchanger (Figure 4, item E).

The heat exchanged was measured with the formula:

$$Q_{cooling} : q\ C_p\ \Delta T$$

where

q = Flow rate of cooling water

C_p = Calorific capacity of water

ΔT = Water temperature increase in the exchanger

For run D012 the heat exchange area was 0.7 m^2. It was replaced in run D013 by another heat exchanger which surface area was 5.9 m^2. The heat exchange values obtained were 7067 $kJ \cdot h^{-1}$ (or 3926 kJ / kg of oil) and 22440 $kJ \cdot h^{-1}$ (or 2117 kJ / kg of oil) for runs D012 and D013 respectively.

For run D012 the rate of liquids condensation at the PCU level was only 1.8 $kg \cdot h^{-1}$ compared to 10.6 $kg \cdot h^{-1}$ for run D013. A problem occurred with the flow control of the recycled oils in run D012. The quantity of heat transferred to the cooling water was greater in run D013 which lasted 5 hours compared to 4 hours for run D012.

The overall heat transfer coefficient for the heat exchanger of quencher # 1 was calculated with the equation:

$$Q_{cooling} = U \cdot A \, (\Delta T)_{ln}$$

where A = heat exchanger surface area

U = overall heat transfer coefficient

$(\Delta T)_{ln}$ = logarithmic differential temperature

The overall heat transfer coefficients calculated for runs D012 and D013 were respectively 121 $W \cdot m^{-2} \cdot ° C^{-1}$ and 142 $W \cdot m^{-2} \cdot ° C^{-1}$.

4.2.4 Heat Exchange Around the Reactor

Eight thermocouples were installed on the external surface of the reactor insulating material (Fiberfrax) in order to measure the global heat transfer coefficient of the reactor with ambient air. We used the formula

$$U_{\text{reactor-ambient air}} = \frac{Q_{\text{loss}}}{A\ \Delta T}$$

where Q_{loss} = heat required to maintain the reactor at the pyrolysis temperature prior the run.

A = external surface of the reactor insulation

$\Delta T = T_{\text{surface,mean}} - T_{\text{ambient air}}$

Results for Q_{loss} and $U_{\text{reactor-ambient air}}$ are presented in Table 4.

TABLE 4: Heat Exchange and Heat Transfer Coefficient for the Reactor in Ambient Air for Runs D011, D012 and D013

Run	Heat Exchange, Q_{loss} (W)	$U_{\text{reactor-ambient air}}$ ($W \cdot m^{-2}\ °C^{-1}$)
D011	3534	7.3
D012	2915	5.6
D013	3639	6.6

For run D012 the insulation was improved with respects to run D011, which explained the smaller amount of heat that was required to bring the reactor to the pyrolysis temperature. For run D013 the calorific losses were more important. The global heat transfer coefficients are similar.

4.2.5 Cooling of the Charcoal Screw Conveyer

The heat of cooling for the charcoal screw conveyer has been calculated based on the same formula used in section 4.2.3.

Quite similar values were obtained for runs D012 and D013: 470 kJ · kg^{-1} and 461 kJ · kg^{-1}, respectively.

4.3 Energy Flowsheets for the Process

The energy balances for runs D012 and D013 are presented in Figures 6a and 6b of the report. The figures summarize the results discussed before. The heat content of the pyrolysis products are also included in these figures.

4.4 Comments on the Reactor Capacity

The volatile matters content of the charcoal recovered from the pyrolysis can be directly related to the degree of conversion of the biomass for the test conditions and the operational parameters used.

Charcoals from runs D012 and D013 have been analyzed. Samples were taken at varying intervals during run D013. The following results were obtained:

FIGURE 6A: Mass and Energy Flows for Run D012

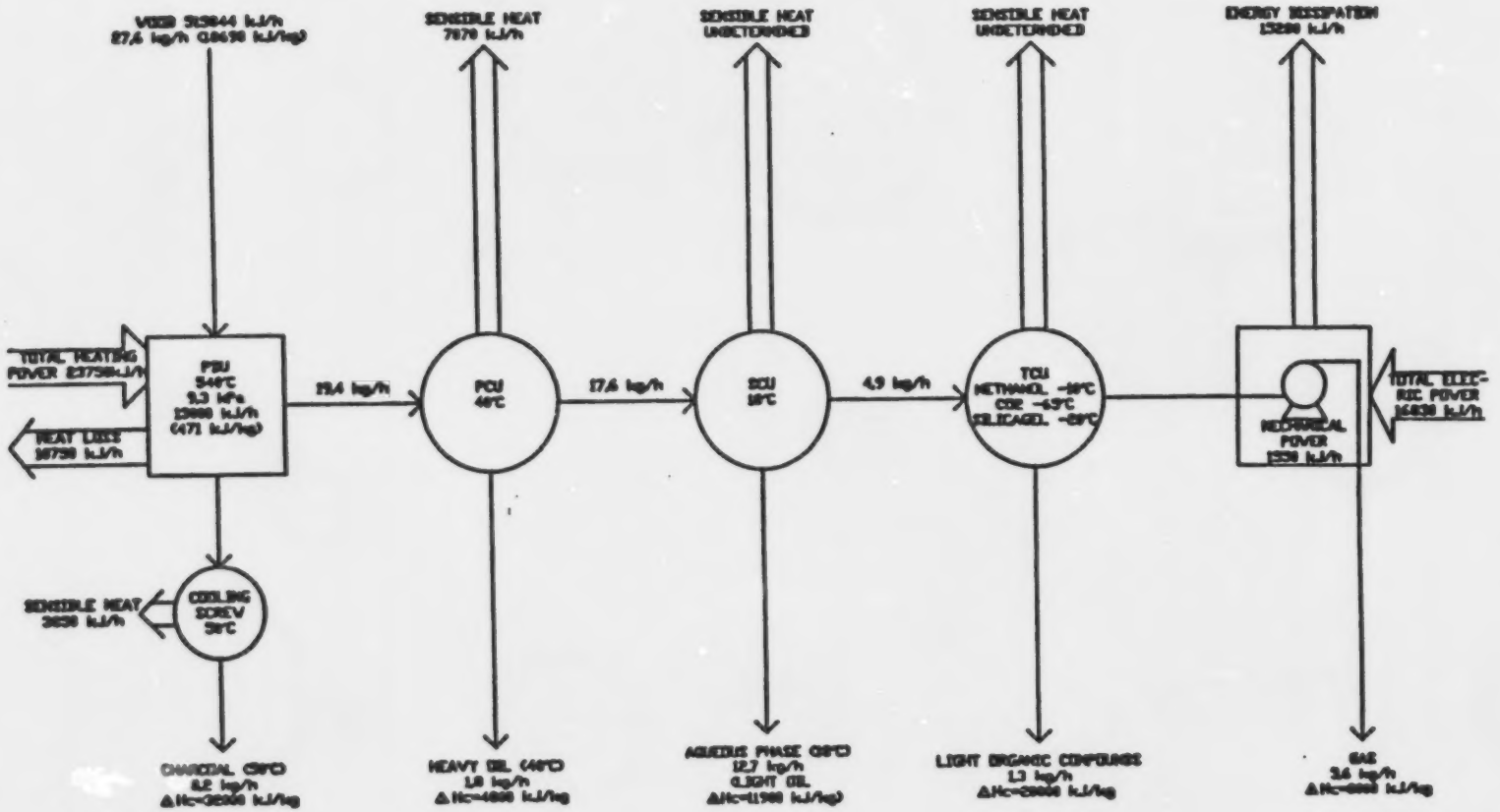


FIGURE 6B: Mass and Energy Flows for Run D013

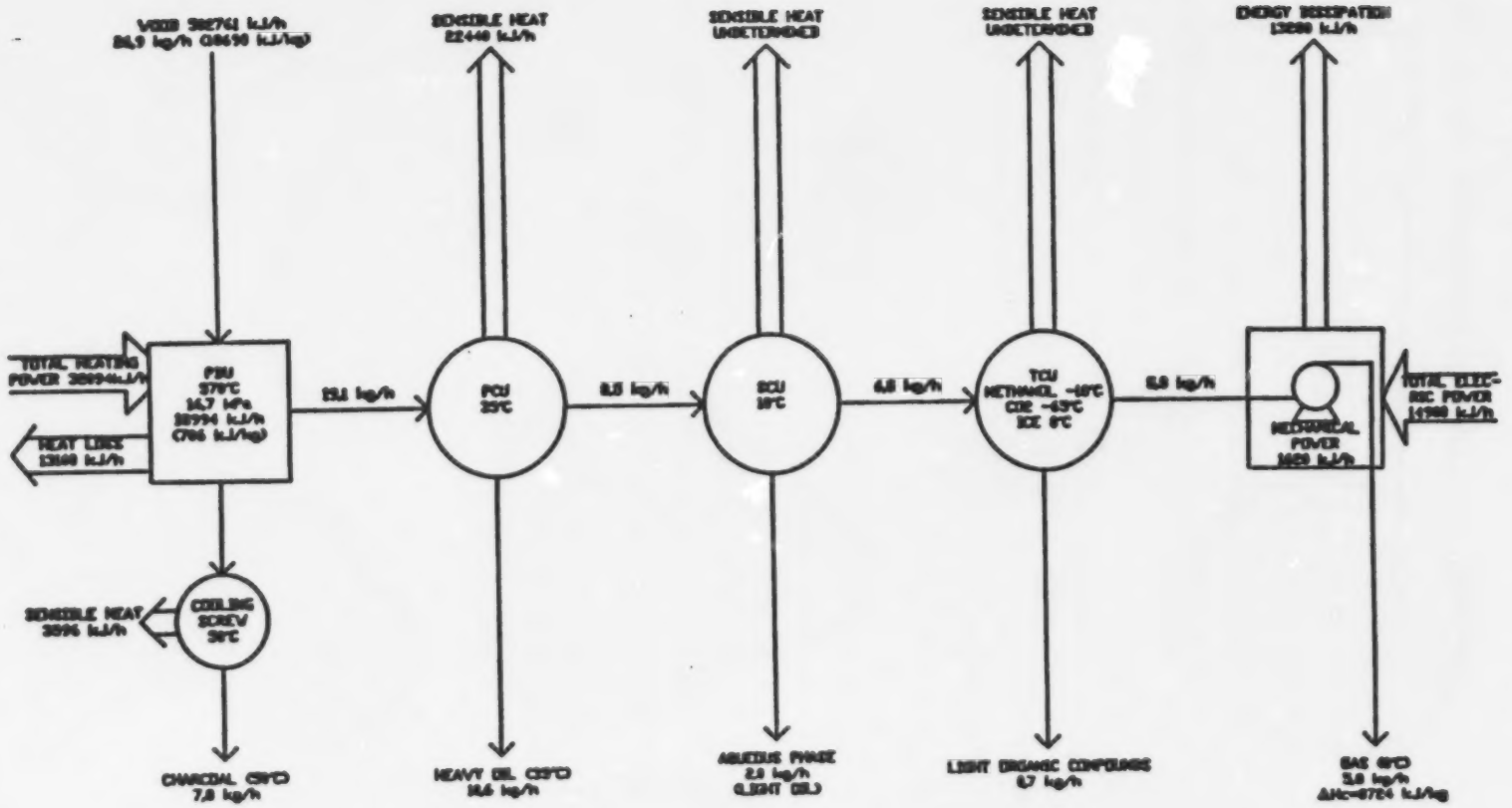


TABLE 5: Charcoal Proximate Analysis for Runs D012 and D013

Run	D012	D013
Volatile Material (wt%)	19.3	33.2
Ashes (wt%)	7.2	5.2
Fixed Carbon (wt%)	73.5	61.6

The high level of volatile matters contained in the charcoal samples for run D013 indicate that the pyrolysis reaction was not completed. It appears that for the test conditions prevailing during this run (16.7 kPa and 570°C maximum temperature), the conversion was comparatively less than for run D012 conducted at 9.3 kPa and a maximum temperature of 560°C. One could expect then from these two experiments that even better results on an oil yield point of view could be obtained at an absolute pressure lower than 9,3 kPa.

Condensation of the pyrolytic vapors with the two quenchers in series, which were operated at 40° and 15° C respectively, was found to be efficient. However, an improved tertiary treatment system should be developed in order to remove traces of water vapor that are still present in the gas stream prior to the vacuum pump.

5.0 PROCESS DESIGN OF A 4000 kg · h^{-1} DEMONSTRATION PLANT

5.1 Initial Hypotheses

This part of the document presents a preliminary evaluation of a 4 t/h (4000 kg · h^{-1}) vacuum pyrolysis plant for wood residues. This study provided the data base for the process scale up. The multiple hearth furnace concept was retained as the pyrolysis reactor. Condensation of the liquid products was similarly performed in quenching towers.

From previous work it was established that the solid biomass material should reach an optimum temperature of 425 to 450°C in order to generate high oil yields. Also the effect of pressure is significant for the decrease or increase of oil yield and for the extent of secondary repolymerization reactions of organic vapors on the charcoal. Since a higher pressure leads to lower oil yield, the pressure was kept as low as possible inside the pyrolysis reactor. An absolute pressure of 4 kPa or less seemed to be adequate. For design purpose we used an absolute pressure of 4 kPa.

Also for economic evaluation it was assumed that wood chips were cut to 25 X 25 X 1.6 mm size and were delivered to the plant site at no cost. In fact this corresponded to the situation encountered in British-Columbia where the forest industry users have to get rid of their wood residues.

A mass balance for the pyrolysis of wood containing 10% humidity and 1.5% ash is presented in Table 6.

TABLE 6
Yields on Pyrolysis of Wood Containing
10% Humidity and 1.5% Ash.

PRODUCT	YIELD (%)
Oil	42
Charcoal	24
Water	25
Gas	9

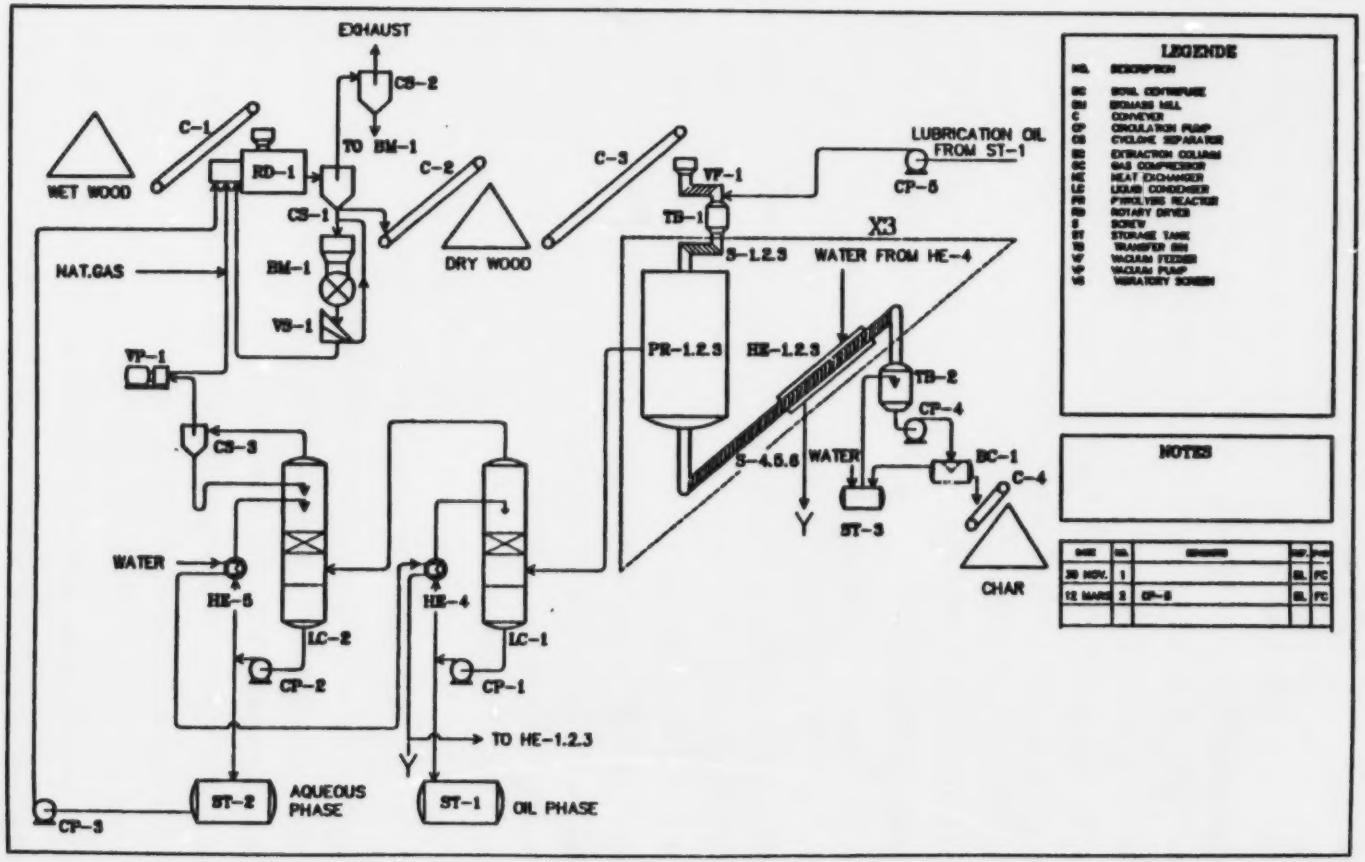
5.2 Process Overview:

As shown in Figure 7, the process proposed in this evaluation consists of first removing moisture from the wood feedstock in a dryer and then pyrolysing wood in a multiple hearth furnace under vacuum. Pyrolytic oil is recovered mainly in the first condensation stage while an aqueous phase composed in a large proportion of water and soluble oil in a smaller extent is condensed in the second condensation stage. Pyrolytic gas gets across the vacuum pump and is burned to generate heat for the dryer. The aqueous phase is also disposed of in the dryer burner. The solid residue is cooled down by direct contact with water before it is pumped out of the system as a slurry to atmospheric pressure. The water and the charcoal are then separated in a centrifuge.

The process can be divided in six different unit operations:

1- Drying of the wood chip feedstock
2- Continuous feeding under vacuum with a screw
3- Wood pyrolysis in the vacuum reactor
4- Condensation of the liquids (oil and water)
5- Vacuum pumping at 4 kPa
6- Cooling and dewatering of the charcoal.

FIGURE 7: Flowsheet of a 4 000 kg h^{-1} Wood Pyrolysis Demonstration Plant



5.2.1 Drying

A multi-pass rotary dryer (RD-1) is used to remove moisture from the wood feedstock, from 50% down to 10%. Operating constraints associated with the dryer impose rigorous sizing of the feed material (25 X 25 X 1.6 mm). The relatively small size chips requirement is attributable to the dryer, not to the pyrolyser. Heat is supplied to the dryer by means of a wood burner furnace that uses sawdust as fuel. The sawdust is generated from the dry wood with a small mill (see BM-1 on Figure 7). Consequently the quantity of dry wood coming out of the dryer corresponds to the sum of both wood to be burned and wood to be pyrolysed. The furnace also burns the pyrolytic gas and the aqueous phase generated during the process (the aqueous phase contains nearly 30% oil). Cyclone separators (C-1 and C-2) are used to collect fine wood particles from the dryer exhaust. A belt conveyer (C-2) carries the dry wood to a 100 tonne capacity storage area.

5.2.2 Continuous Feeding

A vacuum tight screw (SF-1) feeds the dry wood into the pyrolysis system. A small quantity of pyrolytic oil might be necessary to lubricate the wood material and improve its flow across the screw.

5.2.3 Pyrolysis

The multiple hearth furnace configuration was chosen for the pyrolysis reactors. This type of reactor is well suited for heat exchange by thermal radiation which is the predominant mode of heat transfer under reduced pressure. It is also very efficient for solid materials handling since in this type of reactor the material moves from top to bottom by means of rattles. Three units of 1333 kg $\cdot$ h^{-1} capacity each (PR-1.2.3) will operate in parallel to process a total of 4000 kg h^{-1} of dry wood (10% moisture).

Electrical resistors installed inside and at each level of the vacuum reactor are used and act as high temperature radiant heat sources. The final temperature of the charcoal at the exit of the last heating plate was fixed at 425-450°C, which is the optimal temperature range

for maximum oil production. The mean temperature of the organic vapor leaving the pyrolysis reactor will be around 335°C. The vapors are removed from the hot reactive area as soon as they are generated and only a small effect of overheating is expected.

Each of the three reactors will be 2.25 m in diameter and 10 m high with 20 plates or hearths. This represents a total heat exchange surface area of 238 m^2. The design has been made in such a way that it will take one hour for a wood chip particle to get across the 20 reactor hearths (contact time = 1h).

5.2.4 Condensation

The most efficient mode for condensation of vapors when operating at low pressure is by means of direct contact with liquid droplets. This operation is performed in quench towers. In such an unit, cold liquid is sprayed at the top of the column, in a vacuo. The hot vapor to be condensed enters the bottom of the tower and meets, as it moves upward, the cold liquid droplets. Constituents of the vapor that reach their saturation temperature condense and fall in direction of the bottom of the tower. A packed bed made of inert ceramic rings, called "Raschig rings", enhances the contact surface available for heat transfer and increases condensation efficiency. Moreover the drag effect of the liquid trickling down the packed bed of the condenser prevents scaling problem that are common in other types of condensers. The liquid at the bottom is pumped through a heat exchanger to further reduce its temperature before being sprayed inside the column. The liquid overflow is pumped into a storage tank.

The two-stage condensation concept allows to readily separate liquid products that have a higher condensation temperature (heavy oil) from the fraction that has a lower condensation temperature (water and light oil). The oil recovered from the first condensation stage (LC-1) at a temperature between 30 and 40°C is a saleable product. It contains only a low amount of water (3 to 5%) and trace amounts of sulfur (<0.1%). The aqueous phase obtained from the second condensation stage (LC-2) at a temperature between 20 and 23°C may contain a significant quantity of light oil (30%) and other chemicals such as carboxylic acids. This contaminated aqueous phase is eliminated by combustion.

Preliminary evaluation of the condensers shows that LC-1 has a diameter of 2.3 m and a height of 9 m. For LC-2 the calculations lead to a diameter of 1.95 m. It would be probably more economical to build two units with the same dimensions. For that reason LC-2 should have a diameter of 2.3 m and 9 m of height. Also in order to maintain proper operation of LC-1, 30 $L \cdot s^{-1}$ of oil must be pumped by the circulation pump (CP-1) and an exchange area of 135 m^2 for the heat exchanger (HE-1) is necessary. In the case of LC-2, 70 $L \cdot s^{-1}$ of aqueous phase is pumped by CP-2 and the area of HE-2 is 175 m^2. The cooling water requirement for exchangers is 60 $L \cdot s^{-1}$. Note that for economy the same cooling water is used in HE-2 and HE-1 which are in cascades.

5.2.5 Vacuum Unit

As the thermal conversion proceeds an adequate vacuum is maintained in the pyrolysis system by the vacuum pump (VP-1). Another function is to expel the non condensable pyrolytic gas out of the system and to send it to the dryer burner (RD-1).

The vacuum unit consist of a blower stage which raises the pressure from 4 kPa at its inlet up to 10.7 kPa at its outlet. In the next stage a liquid ring vacuum pump brings the pressure slightly over the atmospheric pressure at 106.6 kPa.

5.2.6 Cooling and Dewatering of the Charcoal

The charcoal is taken at the discharge of each reactor by screw conveyers (S-4.5.6) which are cooled by a water jacket (HE-1.2.3) to 150°C. A transfer bin (TB-2) is located at the end of the three screws. Water is sprayed over charcoal to cool it down to the room temperature. Part of this water (50 kg · h^{-1}) evaporates when it gets in contact with the hot charcoal. This steam finds its way out of the system backward through the pyrolysis reactor and the condensation system. Finally a centrifuge pump (CP-4) acts as a vacuum lock and carries the water-charcoal slurry out to the atmosphere. The centrifuge (CB-1) separates the water from the charcoal (the charcoal still contains more than 50% moisture however). The water from the centrifuge is transferred into a storage tank (ST-3) where make-up water is added to account for losses. The water is then once again used to spray the charcoal in the transfer bin (TB-2).

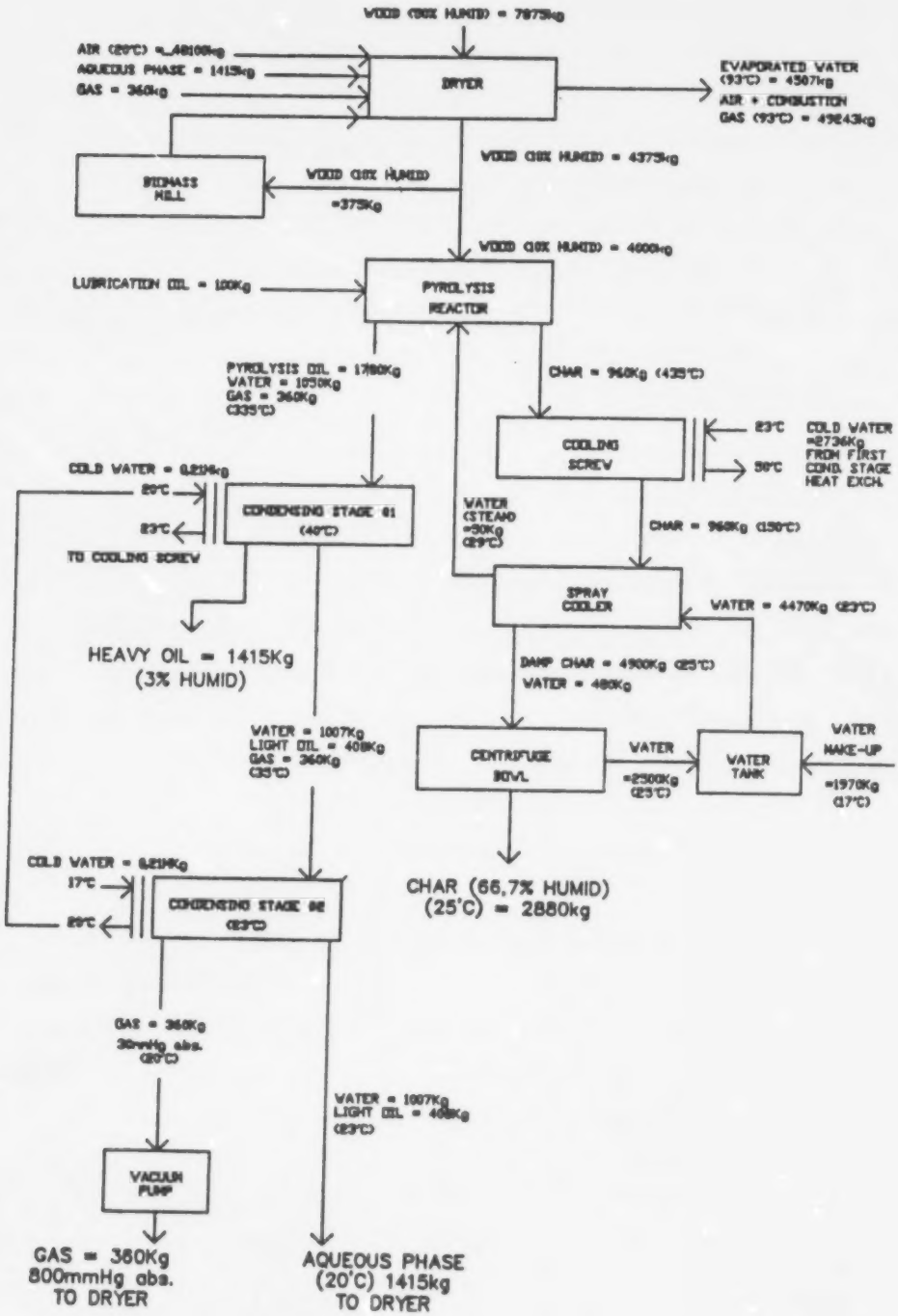
5.3 Mass Balance

The process mass balance is presented in Figure 8 for a plant that would pyrolyse 4000 kg · h^{-1} of wood (10% moisture). This balance shows that 7875 kg · h^{-1} of wood at 50% moisture must be treated to obtain 4000 kg · h^{-1} of wood at 10% moisture. Using ground wood to heat the dryer is probably more economical than buying fuel or natural gas since the only costs encountered are for the drying and for the grinding operations. Nevertheless 375 kg · h^{-1} of wood to be burned represents less than 10% of the 4000 kg · h^{-1} that will be pyrolysed.

Globally there are three inputs to the pyrolysis system:

1- Wood (10% moisture)=4000 kg · h^{-1} |
2- Lubricating oil = 100 kg · h^{-1} | > Total input = 6070 kg · h^{-1}
3- Water make-up = 1970 kg · h^{-1} |

FIGURE 8: Mass Balance of a (one hour basis) 4 000 kg^{-1} Wood Pyrolysis Demonstration Plant



The outputs are the followings:

1- Heavy oil (3% moisture)=1415 kg · h^{-1}		
2- Charcoal (66.7% moisture) = 2880 kg · h^{-1}		>Total output=6070 kg ·h^{-1}
3- Aqueous Phase (29% oil)=1415 kg · h^{-1}		
4- Gas = 360 kg · h^{-1}		

The partial mass balance around the charcoal cooling step shows that the dry charcoal from the pyrolysis reactor (960 kg · h^{-1}) absorbs a lot of water when sprayed in the cooler. Due to its high hygroscopicity the charcoal keeps a large proportion of water even after passing through a centrifuge separator. In fact the moisture content of the resulting wet charcoal reaches 67% by weight. Further drying of the charcoal may be required depending on its final use. Typical properties of the dry charcoal are given in Table 7.

The oil obtained from the condensing stage #1 (LC-1, HE-1 and CP-1) should contain as less water as possible. The capability to operate LC-1 at the right temperature will be very important for the quality and the quantity of the oil product. Properties of the pyrolytic oil are shown in Table 7.

TABLE 7: General Characteristics of Pyrolytic Oils and Charcoal

	OILS	CHARCOAL
Water content (wt. %)	4.4	<1
pH	2.5	
*Pour point (°C)	15	
*Autoignition point (°C)	440	
*Density at 20°C (g/ml)	1.17	
*Viscosity at 40°C (cSt)	250	
*Viscosity at 100°C (cSt)	16.5	
Gross calorific value (kJ/kg, anhydrous basis)	22 500	32 000
Elemental analysis (%)		
C	55.6	84.4
H	5.8	3.5
N	0.7	0.2
S	0.6	0.8
O (by diff.)	37.3	11.1
Proximate analysis (%)		
Ash	0.13	2.8
Volatile Matter		18.5
Fixed carbon		78.7
Specific suface(BET, m^2/g)		≈3

*Test conducted with an oil sample which contained app. 10.7% moisture.

The aqueous phase is condensed at the condensing stage #2. This phase will contain a subtantial quantity of soluble oil which cannot be separated by decantation. Among other products found in this phase are acetic and formic acids. A more complete list is provided in Table 8. During the process the aqueous phase is eliminated in the combusting unit of the rotary dryer (RD-1).

TABLE 8: Typical Organic Compounds Identified in the Aqueous Phase

Formid acid	2-Butanone
Acetic acid	Methanol
Acetaldehyde	Dimethylglyoxal
Methylformate	Crotonaldehyde
Propanal	1-Hydroxy-2-Propanone
Acetone	Furfural
Methylacetate	

5.4 Thermal Energy Balance

Figure 9 illustrates the thermal energy balance for the process. All values were calculated at 20°C. For the pyrolysis reactors a 20% heat loss was assumed in the design. Energy is removed equally from the two condensing stages (~740 kWh · h^{-1}).

The heat of combustion ΔHc of the reactants and the products were taken into consideration to evaluate the thermal energy balance of the process. Values for the heat of

combustion on an anhydrous basis were assumed to be:

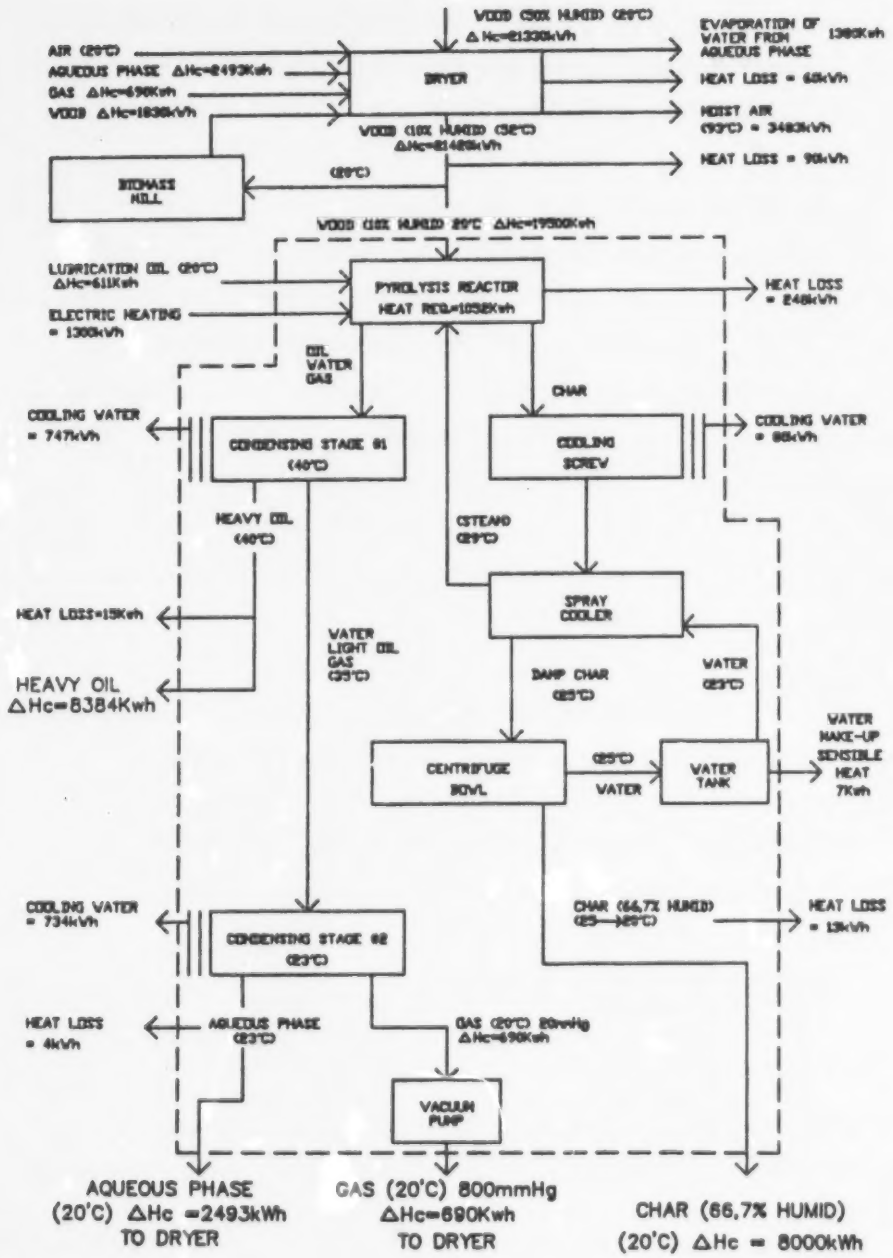
1- Wood = 19500 kJ · kg^{-1}
2- Pyrolytic Oil = 22000 kJ · kg^{-1}
3- Pyrolytic Gas = 6900 kJ · kg^{-1}
4- Charcoal = 32000 kJ · kg^{-1}

For the wood drying operation, the energy required for each kg of water evaporated is 1700 kJ · kg^{-1} of water.

5.5 Equipment Specification

A description of the main equipment units is provided in Appendice 1. Among the most costly equipments are the reactors estimated at 800 k$ each, the dryer at 350 k$ and the vacuum feeder at 500 k$.

FIGURE 9: Energy Balance for a 4 000 kg^{-1} Wood Pyrolysis Demonstration Plant (one hour basis)



6.0 PRELIMINARY ECONOMICS OF A 4 000 kg h^{-1} PLANT

A preliminary profitability study was performed in order to estimate the process sensitivity in terms of profits, based on the market value of the different pyrolysis products obtained. This evaluation was made according to three different scenarios relying on the usages which determined the selling price of the charcoal product.

1- The char is sold as a fuel : $30/tonne
2- The char is sold as metallurgical coke : $75/tonne
3- The char is transformed and used as an activated carbon : $1 000/tonne

For the third scenario a portion of the pyrolytic char is consumed during the subsequent activation step. For that reason we considered that only 30% of the pyrolytic char is left as active carbon and that 70% is burned off during activation.

Also the effect of a tipping fee for the processing of wood residues was investigated.

In all scenarios the oil is sold for $20/barrel and the gas is burned in the dryer. The energy cost is based on electricity cost for British-Columbia in 1990. (Table 9)

TABLE 9: Cost of Electricity in British-Columbia in 1990

Consumption	Rate
Flat rate	$4.09/month
< 270 kWh/month	$0.0781/kWh
< 6000 kWh/month	$0.0577/kWh
< 23000 kWh/month	$0.0426/kWh
> 23000 kWh/month	$0.0276/kWh

Values are presented on a yearly basis for an operation of 4 tonnes per hour during 300 days, 24 hours per day.

6.1 Capacity

Total wood (50% moisture) dried = 56700 t/y
Total wood (10% moisture) burned = 2700 t/y
Total wood (10% moisture) pyrolysed = 28800 t/y
Products: Oil = 10.188 Mkg/y = 8.708 ML/y = 54432 bbl/y
Charcoal (dry) = 6.912 Mkg/y

6.2 Annual Energy Costs

Energy costs are divided in three parts: (basis = one tonne of 10% moisture wood pyrolysed).

1- Wood drying and evaporation of the aqueous phase	= 916 kWh/t
2- Pyrolysis and heat loss	= 325 kWh/t
3- Power (electrical, mechanical)	= 500 kWh/t
Total energy	= 1741 kWh/t
Annual energy cost	= 1.389 M$

An energy saving of 26.4 million kWh is possible if ground wood is used to supply the dryer ($0.0276/kWh) = 0.728 M$

Net annual energy cost = 0.616 M$

6.3 Investment

Investment was calculated for a 4 000 kg · h^{-1} plant including the dryer cost but excluding land and building costs. The fixed Capital Investment (CI) was estimated according to the "Percentage of Delivered Equipment Cost Method" which is valid for such conditions. (2)

6.3.1 Direct Cost

Delivered equipment (DE)= $5.0M

Installation of equipment	39% DE	=	$1.95M
Instrumentation (installed)	13% DE	=	$0.65M
Piping (installed)	31% DE	=	$1.55M
Electrical (installed)	10% DE	=	$0.50M
Equipments peripherical (EP)		=	$4.65M

Total direct cost (DC) = DE + EP = $5.0M + $4.65M = $9.65M

This estimation of DC is valid if buildings, land and land preparation, services (electricity, gas, water) are already available on site.

6.3.2 Indirect Cost

Engineering and supervision, construction expenses	30% DE = $1.5M

Total indirect costs (IC) = $1.5M

6.3.3 **Others**

Contractor fees (7% (DC + IC)) = $0.78M

Total = $0.78M

6.3.4 **Fixed Capital Investment**

(CI) = $9.65 M + $1.5M + $0.78M = $11.93M

6.4 **Profitability of a 4 000 kg · h^{-1} Plant**

6.4.1 **Total Annual Costs**

Sales costs =	$1.408M
Administration costs* =	$1.526M
Total annual costs =	$2.934M

* Including the net annual energy cost.

6.4.2 **Annual Incomes**

Revenues are function of the sale price of charcoal.

TABLE 10: Effect of the Selling Price of Charcoal on the Annual Profit

	Charcoal Utilization		
	Active carbon	Coke	Fuel
Revenues			
Charcoal	$2.246M	$0.518M	$0.207M
Oil	$1.088M	$1.088M	$1.088M
Total annual revenues	$3.344M	$1.606M	$1.295M
Total annual costs	$(2.934M)	$(2.934M)	$(2.934M)
Before tax Profit	$0.400M	$(1.328M)	$(1.639M)

6.5 Profitability with a Tipping Fee

The possibility to impose a tipping fee for the processing of wood chips was investigated. An attempt was performed by adding a tipping fee of $30/tonne of wood containing 50% moisture to the annual revenues ($1.701 M/y). Table 11 summarizes the calculations for the three previous scenarios.

TABLE 11: Effect of the Selling Price of Charcoal on the Profit when a $30 Tipping Fee is Applied (yearly basis)

	Charcoal Utilization		
Revenues	Active Carbon	Coke	Fuel
Charcoal	$2.246M	$0.518M	$0.207M
Oil	$1.088M	$1.088M	$1.088M
Tipping fee	$1.701M	$1.701M	$1.701M
Total annual revenues	$5.035M	$3.307M	$2.996M
Total annual cost	($2.934M)	($2.934M)	($2.934M)
Before Tax Profit	$2.101M	$0.373M	$0.062M

6.6 Comments on the Economic Study

The economic study showed that the 4 000 kg $\cdot$ h^{-1} process will generate profits only if the charcoal is sold as activated carbon. Otherwise operating a plant is marginal since loss will be encountered. From these results it is imperative to upgrade the quality of the charcoal in order to sell it as activated carbon. The objective would be to design and build an activation unit which would improve the charcoal quality to meet the highest activated carbon specifications. An alternate solution would be to get a better price for the oil or extract and sale a few chemical by-products derived from this prior to burning it (see chapter 7 below).

The possiblility to get a $30/tonne tipping fee for wood treatment makes the process more attractive. Break-even calculations show that if the charcoal is sold as coke, a tipping fee of $23.42/tonne (50% moisture in wood) would make it possible to reach the break-

even point. If the tipping fee is increased to $28.91/tonne (wood 50% moisture) or more, then even selling the charcoal as fuel makes the process profitable. It should be noted that in both of these scenarios the annual tipping fee is the most important source of revenues for the process ($1.701M).

It is interesting to note that if the 3 reactors were heated at "no costs" with a small quantity of the pyrolysis oil or charcoal instead of electricity, then savings of about $ 0.2 M per year would be possible. This represents only 7% of the total annual costs. For that reason it seems unlikely at this point that substitution of electric heated reactor for fuel heated reactors would have a significant economical impact. In fact, fuel burners are more appropriate for the drying operation which requires twice as much energy as pyrolysis does. Also the transformation of wood charcoal to active carbon appears far more economically interesting.

7.0 SEPARATION OF CHEMICALS FROM WOOD PYROLYSIS OILS

Wood pyrolysis oils can be considered either as a source of fuel or a source of variety of chemicals, such as rare and commodity chemicals with potential market value.

The use of wood pyrolysis oils as chemical feedstocks is quite different from that of using wood oils as a source of fuels. There are two important reasons. First, the scale of production of chemicals is much smaller than that of fuels. Second, the market price for chemicals is much higher than that of fuels. The extraction of chemicals from wood pyrolysis oils can significantly enhance the overall process profitability.

The characterization and separation of valuable chemicals from wood pyrolysis oils is a very important task, but it is very difficult to achieve, because the chemical compositions of wood pyrolysis oils are rather complex. In reviewing the literature, Pakdel et al (3) found that there are only two general methods which have been reported for the fractionation of wood thermoconversion products into chemical groups: the solvent extraction method and various chromatographic methods.

Pakdel and Roy (4) developed a modified adsorption-chromatography method for the separation of valuable chemicals from hardwood pyrolysis oils . A sequential elution column chromatography was successfully tested to separate wood pyrolysis oil into several fractions (saturates, aromatics, phenolics and polar compounds). The separation had been done first on a small scale column and then scaled up to a large column, which was designed to prefractionate the wood pyrolysis oil into various groups, ideally as an oil purification step prior to preparative HPLC system.

It was concluded that the chromatography separation technology is preferable to the liquid extraction method for the separation of valuable chemicals from wood pyrolysis oils.

7.1 Objective

The objective of this work was to investigate the potential for the separation by liquid chromatography at the laboratory scale of the different chemicals which compose wood

pyrolysis oils. For that purporse a preparative LC system was used to process relatively large quantities of oil (100 g) and then evaluate the feasibility of an industrial unit (600 kg/day).

7.2 Preparation of Pyrolysis Oil Samples

The pyrolysis oil samples were produced in the vacuum pyrolysis Process Development Unit (P.D.U.) during run D010.

The inital feedstock was composed of the white spruce chips (60%) and bark residues (40%) that had been air-dried in a rotary kiln. The feedstock was provided by Biosyn in St-Juste-de-Bretenière, Province of Québec. Table 1 shows a chemical analysis of the white spruce chips used during run D010.

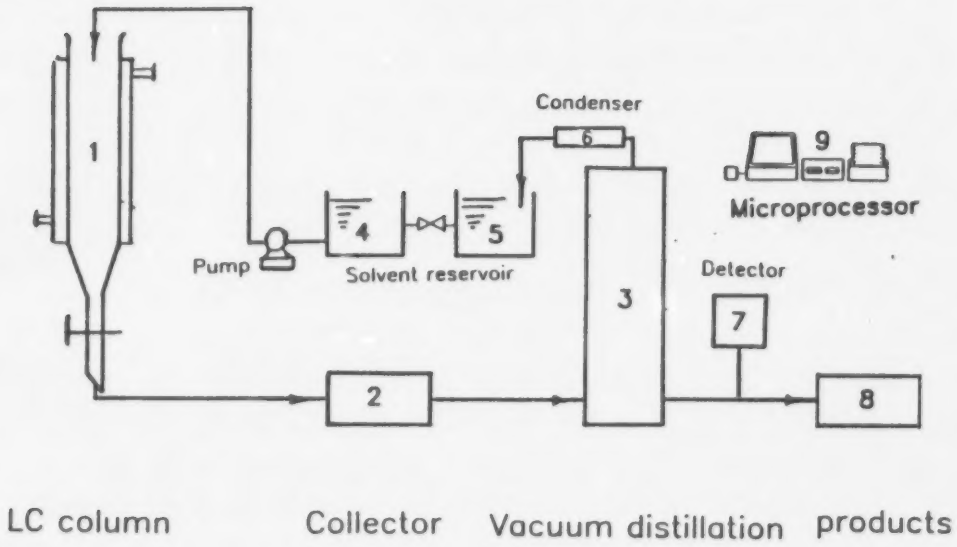
Pyrolysis run D010 lasted 3 hours at a feeding rate of 25 kg $\cdot$ h^{-1}. The mean pyrolysis temperature was 550°C at an absolute pressure of 9.3 kPa. The total oil yield was 45.4% (anhydrous wood basis). The temperature at the primary condensation unit was 20°C. The oil sample used for this LC separation study was collected in the PCU and analysed. The water content of this oil was 20.9%; carboxylic acids accounted for 3.80% of the oil. Some fine carbon particles (0.04%) were also found in this sample.

7.3 Separation of Chemicals by Preparative LC

Following preliminary results obtained using an analytical LC separation column (1 g capacity), a preparative LC separation column with an oil throughout capacity of 100 g was designed.

Figure 10 shows the equipment set-up used in our experiments. A transparent double jacket tube was used to build the preparative LC column. The inside tube was made of a glass column 1250 mm X 75 mm i.d. and 5 mm thick; the outside jacket was made of a plexiglass column 1000 mm X 100 mm i.d. and 5 mm thick. Tap water was circulated into the jacket to maintain constant temperature condition.

FIGURE 10: Schematic of the Preparative Liquid Chromatography Batch Unit



7.3.1 Preparative LC Column Packing

A packing support of 5 to 7 cm high, made of glass wool and white sand (60-120 mesh) was located at the bottom of the column. A slurry method was used to fill the column with silica gel pre-washed with dichloromethane (5).

The water content of the silica gel packing was adjusted to 5.5% by weight. The amount of silica gel needed was approximately 20 to 30 times by weight of the amount sample

to be separated. The height to diameter ratio for the packed bed was approximately 10:1.

7.3.2 Elution and Fraction Collection

In the preparative LC column separation , the solvent sequence illustrated in Table 12 was used depending on the preliminary result of the analytical separation. During the elution process , a typical elution curve was recorded in order to control the separation process and the eluent volume. Six groups were collected according to their functionalities and were subsequently vacuum distilled. The separated fractions were analyzed by GC and GC/MS.

7.4 Preparative LC Column Regeneration

The economic of the separation process highly depends on the volume of solvent and stationary phase used. Therefore, a preliminary investigation which involved regeneration of the eluents used as well as the spent silica gel was made. Solvent regeneration was achieved in the vacuum distillation unit. Regeneration of the silica gel was performed in a Fisher Isotemp Muffle furnace Model 184 A (1.7 kW) at 440 $^{\circ}$ C for five hours under ambient pressure.

7.5 Purification of Rare Chemicals by Thin Layer Chromatography

Further purification of the rare chemicals present in the subfractions, which were collected during the preparative LC separation step, was accomplished by thin layer chromatography.

TABLE 12: Liquid Chromatography Elution Sequence

Group No.	Eluent
1	10% CH_2Cl_2 in petroleum ether
2	40% CH_2Cl_2 in petroleum ether
3	70% CH_2Cl_2 in petroleum ether
4	100% CH_2Cl_2
5	100% Ethyl acetate
6	10% Formic acid in methanol

Purification of the rare chemical compounds was performed on a TLC plate which dimensions were 200 mm X 200 mm. The TLC plate was prepared with TLC standard grade silica gel powder, size 2 - 25 μm (60 A^0 mesh), and BET surface area of approximately 500 $m^2 \cdot g^{-1}$. The silica gel was pre-washed with dichloromethane three times in order to completely remove any trace of impurities. TLC plate preparation procedure was done based on a method described elsewhere (6).

The TLC plate was activated in an oven for 1.5 hours at a temperature of 110 ^oC. Meanwhile a small sample obtained from Group 5 , the most interesting group in this investigation , was precisely weighed and dissolved in 20 % ethyl acetate in dichloromethane. The activated TLC plate was then cooled to ambient temperature and the sample was deposited on it. The developing process was done at 4 ^oC with 20% ethylacetate in dichloromethane.

Once the developing process was over, the separated zones were outlined and carefully scraped from the plate. The individual separated sections were extracted with pure ethyl acetate and separated from the silica gel powder by filtration through a Whatman filter paper No.4. The filtrate was evaporated in a rotary evaporator. Finally, the separated mixture of chemicals were identified and quantified by GC and GC/ MS .

7.6 Preparative LC Column Separation Experiments

7.6.1 Description and Results

The oil sample (run D010) was a mixture of white spruce wood and its bark pyrolysis oil as described earlier. Figure 11 illustrates the GC chromatogram for this pyrolysis oil. Some compounds were identified by MS analysis, but the majority of compounds could not be identified due to the following reasons:

(i) Low concentration
(ii) Complexity
(iii) Low volatility
(iv) Coelution

We found that separation of this oil into a few fractions enhanced GC peak resolution and enabled us unambiguous peak assignments.

The preparative separation of both a 50 g and a 100 g oil samples were performed in the double jacket column. The compounds were fractionated by gradient elution using different polarity solvents. (Table 12)

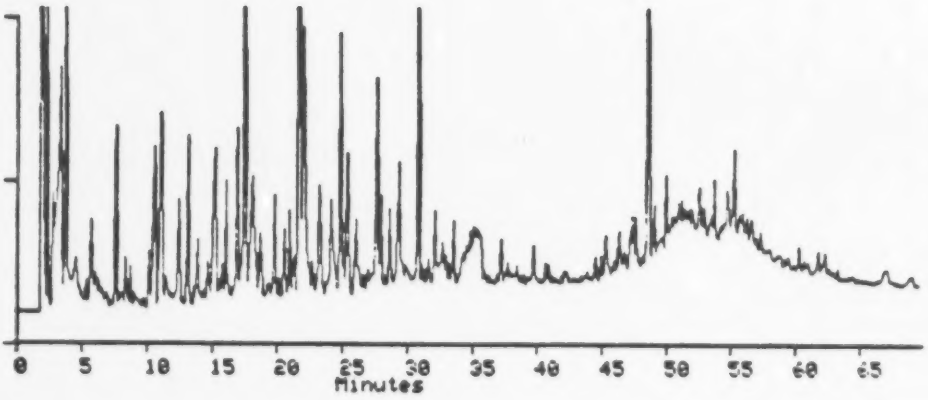
Table 13 compares the methods and conditions used in the 50 g capacity test with that of 100 g.

TABLE 13: Comparison of The Methods and Conditions Used In Preparative LC Separation

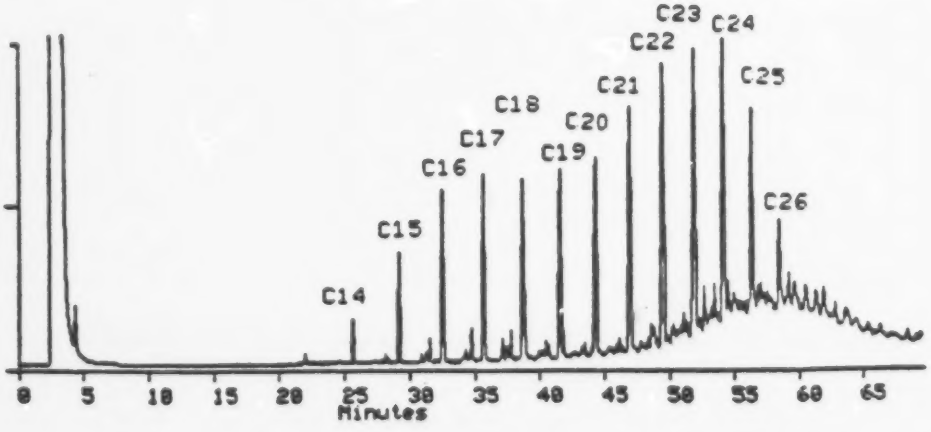
Conditions	Experiments I	Experiment II
Oil Capacity (g)	50	100
Silica Gel (g)	1500	2500
Oil/adsorbent	1:30	1:25
Packing Length (cm)	75.5	119.5
Solvent Volume (ml per group)	4000	8000
Flow Rate ($ml \cdot min^{-1}$)	37	70
Column Inlet Pressure (kPa)	101.3	101.3

The pyrolysis oil samples were fractionated into six groups. Each group was further divided into three to four subfractions to obtain an elution curve, which appeared to be a very useful method for controlling the solvent volume and separation time. Tables 14 and 15 illustrate the results of both preparative separation experiments for softwood pyrolysis oils. GC and GC/MS identification of all subfractions revealed a reproducible separation results.

FIGURE 11: Gas Chromatograms of White Spruce Pyrolytic Oil Fractions

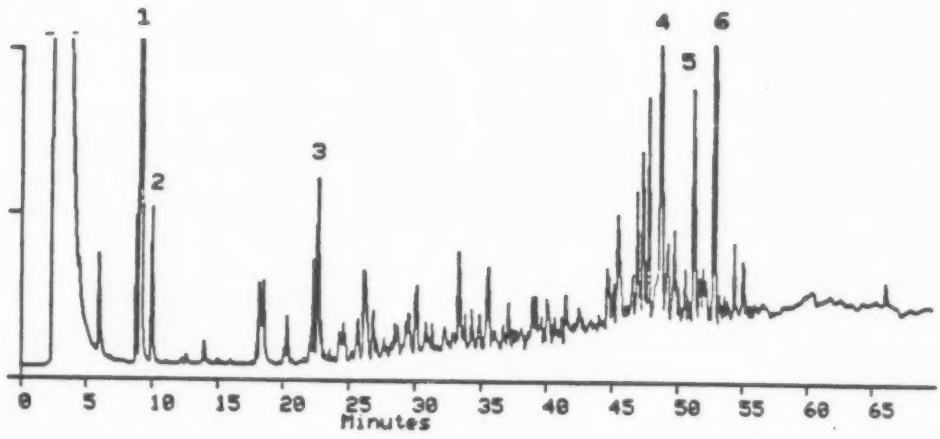


(a). WHITE SPRUCE PYROLYSIS OIL

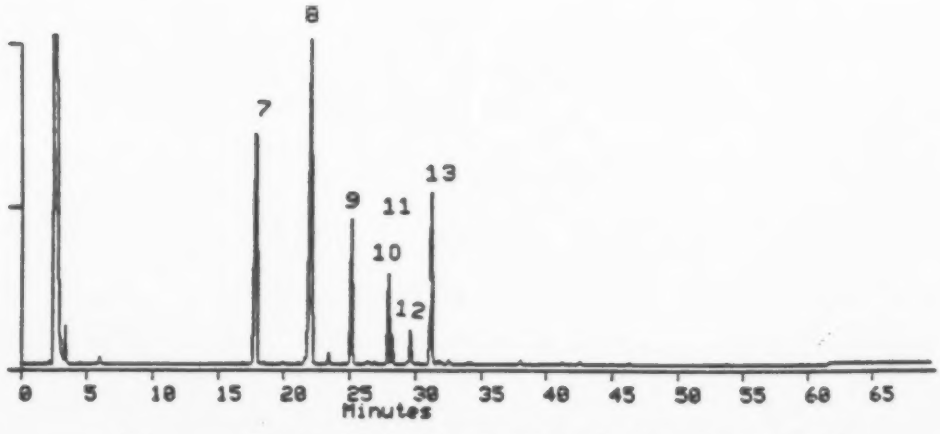


(b). 10 % DICHLOROMETHANE IN PETROLEUM ETHER

FIGURE 11: Gas Chromatograms of White Spruce Pyrolytic Oil Fractions

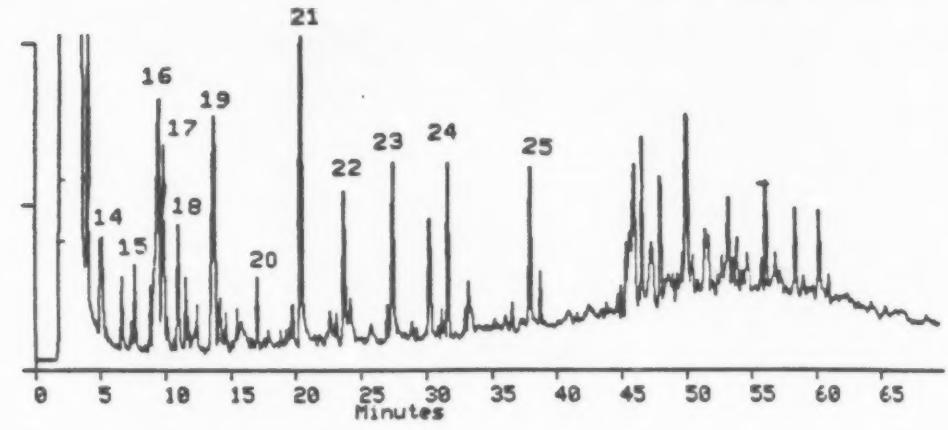


(c). 40 % DICHLOROMETHANE IN PETROLEUM ETHER

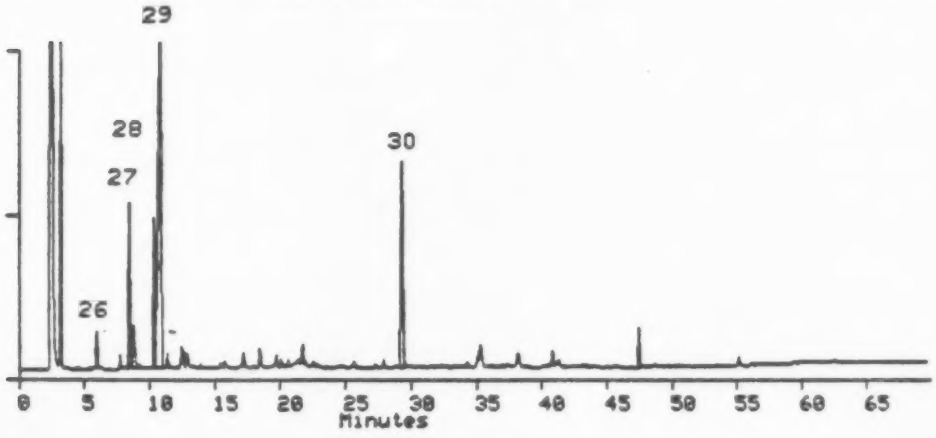


(d). 70 % DICHLOROMETHANE IN PETROLEUM ETHER

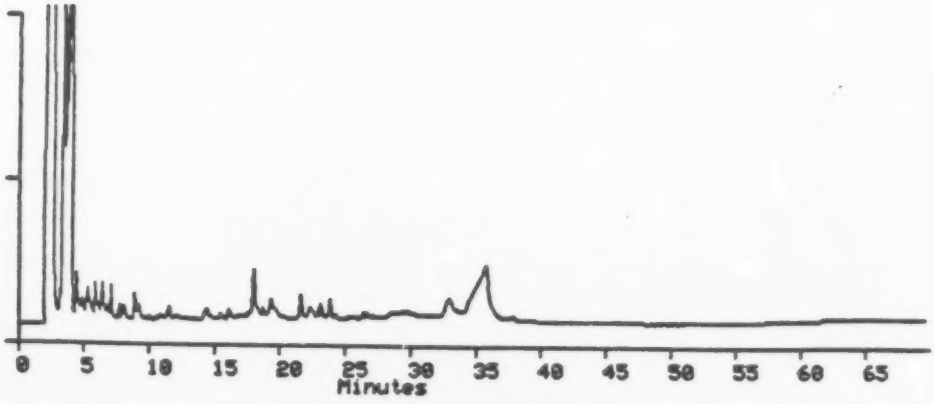
FIGURE 11: Gas Chromatograms of White Spruce Pyrolytic Oil Fractions



(e). 100 % DICHLOROMETHANE



(f). 100 % ETHYL ACETATE



(g). 10 % FORMIC ACID IN METHANOL

TABLE 14: Preparative LC Fractionation Results on White Spruce Oil (50 g Test)

Group No.	Subfraction No.	Flow Rate (ml/min)	Chemicals Collected (mg)	Yield (%) on d.a.f.	Major Compounds Identified in the Fraction
G 1	F 1	50	185.0	0.50	Alkanes C_{14}-C_{26}
	F 2		320.0	0.90	Alkenes C_{14}-C_{26}
	F 3		148.0	0.40	Alkyl benzene
	F 4		127.0	0.30	Alkyl benzene
G 2	F 5	37	202.0	0.50	Alkyl benzene
	F 6		258.0	0.70	2,4-dimethylphenol
	F 7		607.0	1.60	3,4-dimethylphenol
	F 8		283.0	0.80	2,5-dimethylphenol
G 3	F 9	37	595.0	1.60	4-methoxyphenol
	F 10		1078.0	2.90	2-methoxy-4-methylphenol
	F 11		517.0	1.40	Eugenol
	F 12		263.0	0.70	Isoeugenol
G 4	F 13	37	5874.9	15.60	Vanillin
	F 14		1374.4	3.70	Cathecol
G 5	F 15	37	6920.8	18.40	Methylcyclopentenone
	F 16		3611.2	9.60	2(3H)-Furanone
G 6	F 17	30	2456.8	6.50	Carboxlic acids
	F 18		7900.0	21.0	Sugars
	F 19		3685.2	9.80	Polymers
	F 20		1098.0	2.90	
Mass balance			37504.4	99.70	

d.a.f.: dry-ash-free

TABLE 15: Preparative LC Fractionation Results on White Spruce Oil (100 g Test)

Group No.	Subfraction No.	Flow Rate (ml/min)	Chemicals Collected (mg)	Yield (%) on d.a.f.	Major Compounds Identified in the Fraction
G 1	F 1	67	336	0.40	Alkanes C_{14}-C_{26}
	F 2		620	0.80	Alkenes C_{14}-C_{26}
	F 3		286	0.40	Alkyl benzene
	F 4		178	0.30	Alkyl benzene
G 2	F 5	70	316	0.40	Alkyl benzene
	F 6		574	0.80	Cyclohexanol
	F 7		1252	1.70	2,4-dimethylphenol
	F 8		1144	1.50	3,4-dimethylphenol
G 3	F 9	72	1474	2.00	3,4-dimethylphenol
	F 10		1072	1.40	Eugenol
	F 11		2096	2.80	Isoeugenol
	F 12		1284	1.70	4-methoxyphenol
G 4	F 13	72	6104	8.10	0-valerolactone
	F 14		9308	12.40	Cathecol
G 5	F 15	100	9716	13.00	Vanillin
	F 16		4340	5.80	2(3H)-Furanone
G 6	F 17	50	4332	5.80	Carboxlic acids
	F 18		16518	22.0	Sugars
	F 19		11893	15.80	Polymers
	F 20		2013	2.70	
Mass balance			74856	99.50	

d.a.f.: dry-ash-free

Group 1:

Group 1 was mainly composed of straight-chain hydrocarbons, dominated with alkanes and alkenes ranging from C_{14} to C_{28} carbon numbers. The chromatogram exhibited a characteristic series of double peaks. The peaks with the shorter retention time were identified as alkenes, and the other peaks were alkanes. In addition , some branched chain saturated hydrocarbons and some substituted aromatic compounds were identified in this group.

Group 2:

This group contained many aromatic type compounds eluting between 35--57 min retention time. Most of them were in the alkyl benzene series but a few phenolic compounds were also found in this group.

Group 3:

Six major peaks were observed in this group. The major components eluted between 14-25 min retention time.

These peaks were mainly composed of phenolic compounds,which were further confirmed by GC / MS. Only two compounds exceeded the 0.5% by weight concentration limit, including 2-methoxy-4-methylphenol and 4-methoxyphenol.

Group 4:

This group was composed of polar oxygenated compounds such as aldehydes, cycloketones and highly complex ester compounds. Most components were eluted between 5 to 37 min retention window. In addition some other highly complex oxygenated compounds were eluted in the retention window between 45 to 57 min; these could not be identified by GC/MS.

Group 5:

This group was similar to Group 4. The major peaks represented oxygenated compounds. It was mainly composed of cycloketones and vanillin. The most interesting discovery of Group 5 was the detection of 2-methylcyclopenten-1-one and 2 (3H)-furanon; their respective concentration exceeded 0.5% by wt on an anhydrous and acid-free oil basis. In this group only vanillin (4-hydroxy-3-methoxybenzaldehyde) was found in concentration above 1 %.

Group 6:

This group was composed of strongly polar compounds such as sugar and polymers, which showed no significant response on GS/MS . However the yield for this group reached 44% by weight on an anhydrous and acid - free oil basis. This indicated that most compounds present in wood pyrolysis oils were highly polar and non volatile compounds. These compounds probably could be further transformed into different detectable compounds, for example by hydrolysis.

All chromatograms for these groups are shown in Figure 11. The major peaks were identified and listed in Table 16.

7.6.2 Mass Balance

The total mass balance for the preparative LC separation tests was calculated for white spruce wood pyrolysis oil (Run D010) and it was close to 100% in both tests.

Figure 12 represents a summary of the mass balance calculation for the preparative separation of 100 g oil (as-received basis) by Liquid Chromatography (LC). Solvents were recovered by vacuum distillation. Group 4 and Group 5 were combined as one group G 4 + G 5 due to their similar composition.

FIGURE 12: Mass Balance for Preparative LC Separation

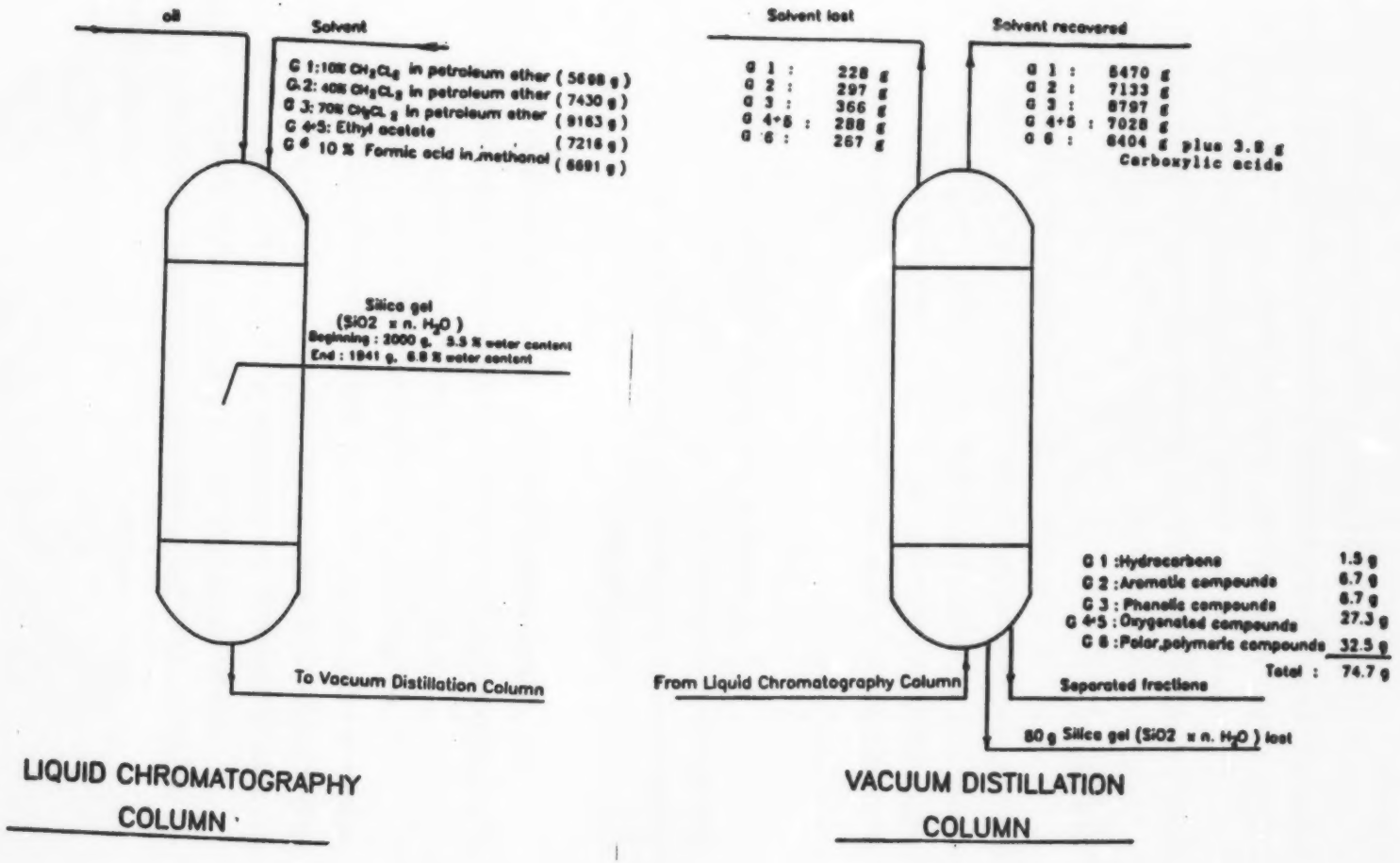

oil
Solvent
G 1:10% CH_2Cl_2 in petroleum ether (5698 g)
G 2: 40% CH_2Cl_2 in petroleum ether (7430 g)
G 3: 70% CH_2Cl_2 in petroleum ether (9163 g)
G 4+5: Ethyl acetate (7216 g)
G 6 10 % Formic acid in methanol (6691 g)
Silica gel
(SiO_2 x n. H_2O)
Beginning : 2000 g. 3.5 % water content
End : 1941 g. 6.8 % water content
To Vacuum Distillation Column
LIQUID CHROMATOGRAPHY
COLUMN
Solvent lost
G 1 : 228 g
G 2 : 297 g
G 3 : 366 g
G 4+5 : 288 g
G 6 : 267 g
Solvent recovered
G 1 : 6470 g
G 2 : 7133 g
G 3 : 8797 g
G 4+5 : 7028 g
G 6 : 6404 g plus 3.8 g Carboxylic acids
From Liquid Chromatography Column
G 1 :Hydrocarbons 1.5 g
G 2 :Aromatic compounds 6.7 g
G 3 : Phenolic compounds 8.7 g
G 4+5 : Oxygenated compounds 27.3 g
G 6 :Polar,polymeric compounds 32.5 g
Total : 74.7 g
Separated fractions
80 g Silica gel (SiO_2 x n. H_2O) lost
VACUUM DISTILLATION
COLUMN

TABLE 16: Compounds Identified in White Spruce Pyrolysis Oil

Fig. 11 Peak No.	Retention time	Assignment
1	9.17	1,2-dimethylbenzene
2	10.00	1,3-dimethylbenzene
3	22.67	4,7-dimethylbenzenofuran
4	48.75	2,5-dymethylphenanthrene
5	51.33	2,3,5-trimethylphenanthrene
6	51.92	2-(1,1-dimethylethyl)anthracene
7	17.92	4-methoxyphenol
8	22.08	2-methoxy-4-methylphenol
9	25.17	4-ethyl-2-methoxyphenol
10	28.00	2-methoxy-4-(2-propyl)phenol
11	28.25	2-meyhoxy-4-(1-propyl)phenol
12	29.67	Vanillin
13	31.25	2-methoxy-5-(1-propyl)phenol
14	5.17	Acetol
15	6.67	3-hydroxy-cylohexanone
16	9.50	2(3H)-Furanone
17	9.83	2-Methylcyclopentenone
18	11.00	Butyrolactone
19	13.75	5-methylcyclohexanone
20	17.08	0-valacrolactone
21	20.50	1,2-Benzendiol
22	23.75	3-methyl-1,2-benzendiol
23	27.50	Hydroquinone
24	31.75	4-hydro-3-methylbenzoic ester
25	38.08	Syringaldehyde
26	6.00	2,5-dimethylfuran
27	8.50	6-methyl 3(2H) pyridazinone
28	10.33	2-Cyclopenten-1-one
29	10.83	2(3H) furanone
30	29.33	Vanillin

Methanol, due to its high polarity, dissolved some silica gel during the last elution of the separation process. At the end the weight of silica gel was mesured. We found that approximately 80 g of anhydrous silica gel was lost in Group 6. Most of the lost silica gel was recovered from Group 6 by solvent dissolution and filtration. Also the water content of the siliga gel increased from 5.5% up to 6.8%; this was attributed to the absorption of water contained in the pyrolysis oil sample, by the silica gel particles.

The elutate from each group was transferred into a vacuum distillation column (Figure 12) in order to recover the eluent and isolate the products. During the distillation process, approximately 4% of the solvents was lost.

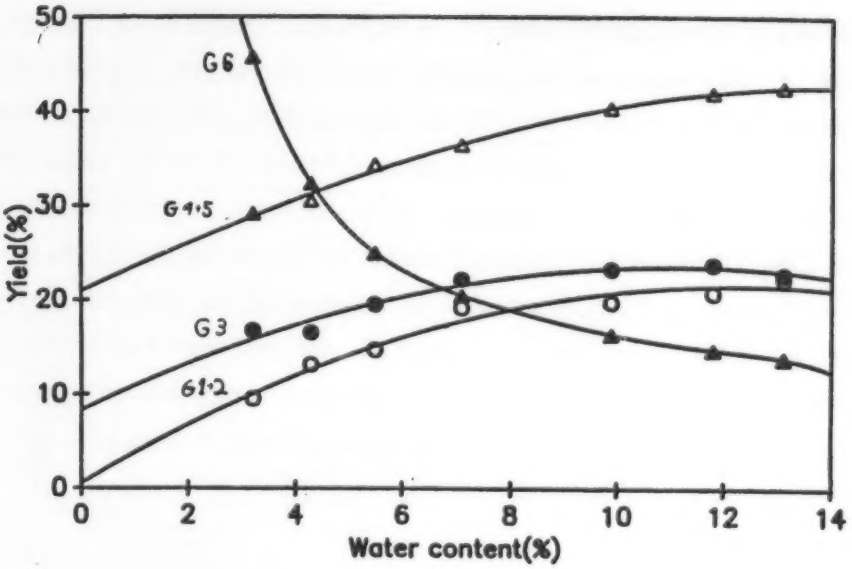
In summary , preparative liquid chromatography separation of 100 g (as-received basis) over 2 kg silica gel produced various chemicals including 1.5 g hydrocarbons, 6.7 g aromatic compounds, 6.7 g phenols, 27.3 g oxygenated compounds and 32.5 g polymeric compounds. The separation requested approximately 36 kg of solvents. More than 96 % of the eluting solvents was recovered by vacuum distillation . The spent silica gel was regenerated and reused. 4 % of silica gel was lost during the regeneration process.

7.7 Effect of Silica Gel Activation on LC Separation

The effect of the silica gel moisture content on the preparative LC separation was studied in the range of 3.2 % to 13.1 % (by weight). In order to reduce the amount of elution solvents used and in order to reduce the separation time, only four groups were collected during this particular set of experiments, i.e:

Group 1 + 2:	40 % dichloromethane in petroleum ether
Group 3:	70 % dichloromethane in petroleum ether
Group 4 + 5:	Ethyl acetate
Group 6:	10 % formic acid in methanol

FIGURE 13: Effect of Silica Gel Water Content on Separation Results



All other separation procedures were the same as those stated previously. Figure 13 shows the experimental separation results using different silica gel moisture contents. The individual fractions in each experiment were strongly affected by the silica gel water content. For example, the yield of Group 1 + 2 had a strong tendency to increase with the increase of silica gel water content. The reason was that Group 1 + 2 was mainly composed of non polar hydrocarbons , which had low affinity to the silica gel surface, even in the case of very active silica gel (e.x. 3.2 % water content). As the silica gel activity decreased, the equilibrium of hydrocarbons between the moving phase and the stationary phase was broken, and compounds desorbed into the moving phase and washed down the column. The results were confirmed with GC and GC/MS analyses. Although Group 1 + 2 yield for silica-gel with 13.1 % water content was twice that of siliga-gel with 3.2 % water content, the column resolution of the former run was not as good as for the latter.

Group 3, which was mainly composed of less polar aromatic compounds and medium polar phenolic compounds, showed similar results as Group 1 + 2. due to its high polarity, Group 4 + 5 (oxygenated compounds) was strongly adsorbed on the silica gel silanol surface. Even though silica gel activity was decreased, stronger solvent (ethylacetate) was still needed for the separation of this group. Consequently Group 4 + 5 yield was increased as the silica gel activity decreased (Figure 13). As it was expected, Group 6 yield was decreased. Experiments showed that under the lowest silica gel activity (e.g. 13.1% water content), only 14.7% of compounds eluted in Group 6. As we know, the total oil contained 6-7% low molecular weight carboxylic acids, and 5-6% sugars. It is therefore expected that this oil contains approximately 2% high polar compounds other than carboxylic acids and sugars, which are soluble in 10% formic acid in methanol. In contrast, Group 6 yield reached 44.4% on an anhydrous and acid-free basis with highly active silica gel (3.2% water content). It could be concluded from these results that the softwood pyrolysis oil contains approximately 31% of oxygenated compounds with higher polarity than that of typical oxygenated compounds such as vanillin present in Group 4 + 5, which are also soluble in 10% formic acid in methanol.

7.8 Effect of Elution Solvent Volume on LC Separation Results

Attemps were made to reduce the solvent volume used as much as possible and decrease also the elution time without disturbing the column resolution and products yield.

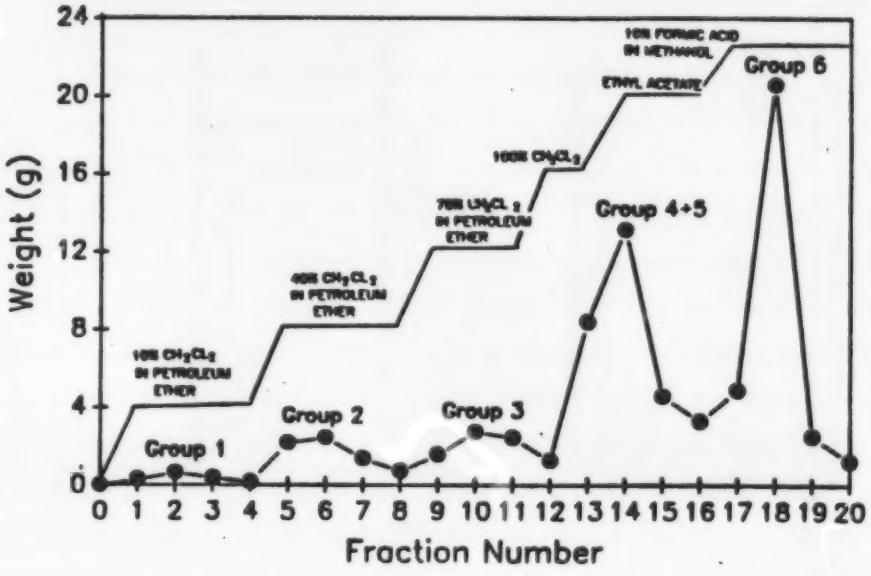
Usually three hypotheses can be considered to reduce the elution solvent volume:

(1) Increasing the elution solvent polarity, using more polar solvents.
(2) Enlarging the concentration differences between two successive elution solvents.
(3) Combining the fractions collected by the analytical LC column into groups that would represent a chemical class of compounds having similar chemical functionalities.

Preliminary tests showed that the first hypothesis cannot result in an apparent reduction in solvent volume and it frequently resulted in poor resolution. The second and third hypotheses were simultaneously tested.

In an experiment twenty individual fractions were collected and analysed. The results presented in Figure 14 show that it is possible to combine the twenty fractions according to their chemical classes.

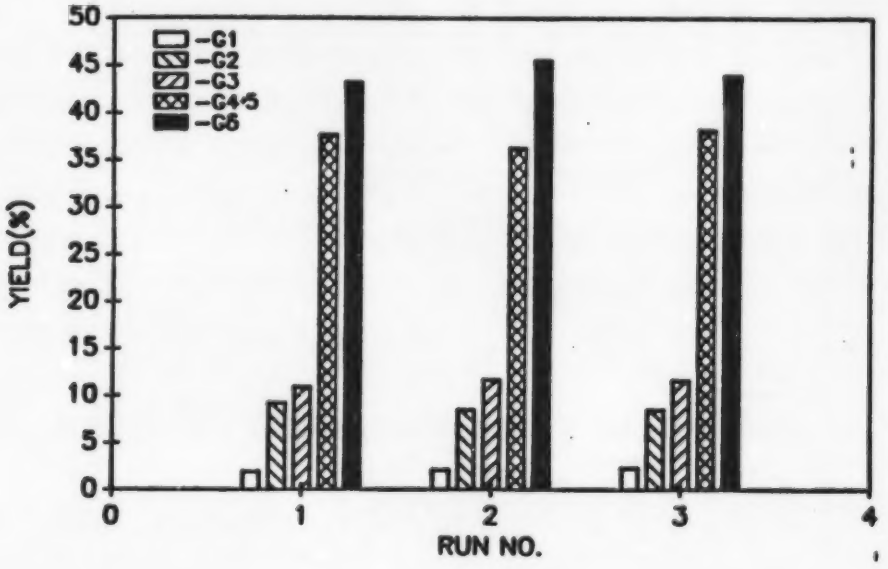
FIGURE 14: Typical Preparative Liquid Chromatography Column Elution Graph



Fractionation of pyrolysis oils into aliphatic or alicyclic hydrocarbons (corresponding to the previous Group 1), aromatic hydrocarbons (Group 2), monophenolics (Group 3), aldehydes, ketones and diphenolics (Group 4 + 5) and carboxylic acids, sugars (Group 6) was achieved. The experimental results showed that the preparative LC column separation was significantly affected by the elution solvent volume and polarity. However, we found that approximately 40% to 50% of the elution solvent volume could be reduced by using the third hypothesis mentioned earlier without significant changes in the column resolution, selectivity and product yield.

Figure 15 shows that the preparative liquid chromatography separation can be repeated and is very reproducible with less than 5% discrepancy.

FIGURE 15: Reproducibility of Preparative LC Separation



7.9 Efficiency of Regenerated Silica Gel

The regeneration of silica gel by burning at high temperature (400-600°C) in a furnace was tested. The physical appearance of the regenerated silica gel was similar to the fresh silica gel. Since the silica gel particles were crashed under high temperature, therefore the specific surface area was expected to change considerably. The regenerated silica gel showed less activity than the fresh silica gel, due to the chemical alteration by highly polar solvents, such as formic acid.

The regenerated silica gel was cooled at room temperature, washed with dichloromethane and then exposed to ambient air for about 48 hours before feeding into the preparative LC column. The regenerated siliga gel activity was adjusted to 4.6% water content by the addition of a predetermined amount of pure water.

The sequential elution chromatographic experiment with the regenarated silica gel and solvent was done in the preparative LC column under the same elution process parameters as those used with the fresh silica gel.

Table 17 compares the fractionation results in both fresh and regenerated silica gel. A fairly good reproductibility was achieved in both experiments, except for Group 5. Group 5 chromatogram of the regenerated silica gel was quite different from that of fresh silica gel, which was presumably due to the low regenerated silica gel activity. It seemed that the major compounds in Group 5 (e.g. vanillin and cyclopenten-1-one) were washed out in advance in Group 4 and overlapped with the bulk of oxygenated compounds as it was observed from the chromatograms. Moreover, some highly polar polymeric compound belonging to Group 6 were eluted in Group 5, resulting in a high yield. This implied that the low silica gel activity could accelerate the elution of organic compounds off the liquid chromatography column and reduce the possible silica gel molecular structure damage and operation cost. In some cases, the application of low active silica gel could significantly reduce the elution solvent volume and operation time and cost. However, in all cases mentioned above, the column resolution and column selectivity were fairly satisfactory.

The key problem of silica gel regeneration is related to the process economics and sometimes to its quality. The preliminary regeneration cost estimation of the used silica gel was approximately $1.50 for 1 kg of siliga gel on the laboratory scale. However fresh siliga gel is usually sold for $5.50 per kg. Advanced silica gel regeneration method is under investigation in our laboratory.

TABLE 17: Comparison of LC Separation Using Fresh and Regenarated Silica Gel

Group	Elution Solvent Volume (L)		Flow rate ml/min		Received Separate Products (mg)		Recovery on raw oil basis (%)	
	Fresh	Reg.	Fresh	Reg.	Fresh	Reg.	Fresh	Reg.
G 1	10	10	67	68	1775.5	1972.7	1.8	2.0
G 2	10	10	70	77	1166.6	1364.6	1.2	1.4
G 3	10	10	70	80	4127.8	4079.1	4.1	4.1
G 4	10	10	100	100	5017.4	4355.0	5.0	4.4
G 5	8	8	100	100	27806.0	30900.0	27.9	30.9
G 6	7	7	60	60	38288.7	36300.0	38.2	36.3
Total					78180.0	78970.0	78.2	79.0

* Oil/Silica gel ratio = 1:20
Water content of fresh silica gel = 4.31%
Water content of regenerated silica gel = 4.6%

7.10 Purification of Rare Chemicals by Thin Layer Chromatography

Further purification of the rare chemical compounds derived from Group 5 eluted with ethyl acetate was performed on a thin layer chromatography plate.

Group 5 is mainly composed of complex oxygenated compounds with high polarity. Its chromatogram is shown in Figure 11 f.

A typical developed TLC plate had (six) distinct separated bands. Visualization under ultraviolet lamp showed that each band contained one or two chemicals. Those bands were scratched from the TLC plate and extracted with 100% ethyl acetate to remove the chemicals. Purified chemicals were separated after filtration and analyzed by GC/MS.

Table 18 lists Rf values of a few chemicals purified on TLC plates.

TABLE 18: Purification of Rare Chemicals of Group 5 (eluted with ethyl acetate) by Thin Layer Chromatography

Band No.	Rf	Assignment	Yields (%) on w.a.f. *
B 1	0.90<Rf<0.99	Phenolic compounds	0.20
B 2	0.87<Rf<0.90	Isoeugenol	0.20
B 3	0.75<Rf<0.83	2(3H)-Furanone	0.52
B 4	0.67<Rf<0.72	Vanillin	1.50
B 5	0.22<Rf<0.62	Unknown	0.90
B 6	0.02<Rf<0.17	Ethanone	0.20
B 7	0.00<Rf<0.02	Benzyl butyl phthalate	0.50
Total			3.52

(*) w.a.f.: water and acid free oil basis

8.0 PRELIMINARY FEASIBILITY STUDY OF THE PREPARATIVE LC SEPARATION METHOD

A preliminary economical study of the preparative LC separation of chemicals from wood pyrolysis oils was made to estimate the feasibility of the separation process developed in our laboratory. The feasibility study also included the cost of recycling or regenerating stationary phase and the eluents.

The following assumptions were made:

(1) Operation would proceed with three shifts per day.
(2) The production capacity of the pyrolysis oil feedstock is approximately 600 kg per day, at the pilot plant scale.
(3) The loss of elution solvents and silica gel during the regeneration process is specified at 0.1%.
(4) The selling prices of the products are representative values of certain classes of compounds.

Tables 19 and 20 present the preliminary economics of the LC separation process. From this analysis it appears that solvents and silica-gel represent more than 50% of the costs. ($1950/$3560). Moreover the cost of solvents and silica-gel is greater than the total revenues. Therefore the process, as it is presented, is not profitable. Selling the products as gross hydrocarbons, phenolics, etc... is not attractive. More intensive separation must be done in order to extract pure substances with improved market values.

TABLE 19: Preliminary Estimation of Pilot Plant LC Separation Costs

Parameters	Amount required	Economic life (years)	Unit cost ($/day)
Oil Cost	600 kg (anh/d)		96
Fixed capital investment			
- Equipments	1.1 M $	10	308
- Building	0.15 M $	20	20.5
- Solvents and silica gel	2.0 M $ 0.1% lost daily		1950
Solvents recovery fees	(10% of process cost)		308
Operation costs			
- Labor-related	6 persons/day at 10$/hour		480
- Supervision	1 person /day at 15$/hour		120
Utilities			
- Water	200 tonnes at 0.12$/tonne		24
- Electric power	1000 kWh at 0.04$/kwh		40
Maintenance and supply materials	5% of total investment		108
Unexpected expenses	5% of total investment		108
Total costs			3562.5

TABLE 20: Total Income From Recovered Chemical Fractions
(600 kg/day capacity)

Fraction	Yield (%) on w.a.f.	Quantity (kg)	Price (*) ($/kg)	Income ($/day)
Hydrocarbons	13.1	78.6	1.39	109.3
Phenolics	16.5	99.0	6.7	663.3
Oxygenated compounds	21.1	126.6	4.8	607.7
Polar compounds	49.1	284.6	1.6	471.4
Total incomes ($/day)				1851.7
Total expense ($/day)				3562.5
Profit (deficit) ($/day)				(1710.8)

W.a.f.: water and acid free oil basis

(*) Average value is adapted from U.S. Chemical Market (1985).

Table 21 lists some of the valuable chemicals identified with their yields. The market values of these chemicals are also presented in the Table. It should be pointed out that the valuable chemicals listed in Table 21 are not the only ones which could make the process feasible. There are large proportions of low molecular weight carboxylic acids present in wood pyrolysis oils (7) as well, which could also significantly contribute to the profitability of the LC separation process.

The separation process economics can also be significantly improved if the separation was performed on a Preparative High Performance Liquid Chromatography (HPLC) system. HPLC can significantly reduce the solvent volume in comparison with batch LC process.

TABLE 21: Major Valuable Chemicals Detected in Wood Pyrolysis Oils

Chemical	Typical use	Price (US$/kg)	Yield(%) on w.a.f. *
Cyclohexanone	Organic synthesis	1.21-1.28	0.1
Ethylbenzene	Solvent	0.51	0.01
Allyl alcohol	Solvent/reactive	1.98	0.01
Phenol	Disinfectant	0.79-0.93	0.6
m-cresol	Disinfectant	3.76	0.3
o-cresol	Photography	1.91	0.3
p-cresol	Phenolic resin	1.90	0.3
Eugenol	Analgesics	8.59-12.89	0.1
Furfural	Germicide	1.59	0.05
Guaiacol	Pharmaceutical industry	5.95	1.4
Isoeugenol	Chemical industry	11.69-12.33	0.62
Resorcinol		3.96	0.4
Catechol	Photography	7.93	1.99
Butyrolactone		2.40	0.05
Vanillin	Flavoring agent	13.75	2.91
2(3H)-Furanone	Pharmaceutical industry	(**)	0.5
2-methylcyclopentenone		(**)	0.2
Hydroquinone		(**)	0.4
Syringol		(**)	1.50
4-tert-Butylcatechol		(**)	2.25

(*) w.a.f. water and acid free oil basis

(**) No price available

9.0 COMMENTS ON LC SEPARATION OF WOOD PYROLYTIC OILS

Several valuable chemicals were identified in the wood pyrolysis oil. These chemicals were separated in different groups by a LC technique. The reproductibility of the method was good with approximately 5% difference. A good separation was also obtained with the regenerated sicila-gel.

The feasibility study of a 600 kg h^{-1} wood oil plant showed that major improvements will be required to reach profitability. Better solvent recovery and better silica-gel regeneration, or the use of more efficient separation techniques than LC (such as HPLC or membrane technology) should be investigated to obtain a better performance and lower operation costs.

10.0 VACUUM PYROLYSIS OF REFUSED DERIVED FUELS (RDF)

10.1 State of the Art

Municipal solid waste (MSW) is a significant potential renewable feedstock for thermochemical conversion to liquid and gaseous products. A review of pyrolytic conversion systems for MSW made by Kuester (8) showed that little progress has been made up to now in that field. The main reasons are the heterogeneous nature of MSW and the complex composition of the liquid obtained by pyrolysis which make analytical identification studies difficult.

The composition and properties of the liquid products will govern their end use as chemicals or else as liquid fuel. For that reason, the determination of relative amounts of compound classes is of prime importance.

10.2 EXPERIMENTAL

10.2.1 Feedstock

Refused Derived Fuels (RDF) were prepared from MSW produced in Ville de Laval, P. Qué. The RDF briquettes were compressed at a temperature of 170°C. The outlet temperature was 110°C. The briquettes in form of bricks were broken in smaller pieces (1/8" - 1/2") prior to feeding the batch pyrolysis reactor. The proximate analysis of the initial feedstock gave 59.8% volatile matters, 29.1% ash and 11.1% fixed carbon. The sample moisture content was 3.1%.

10.2.2 Vacuum Pyrolysis Experiments

The vacuum pyrolysis experiments were performed in a 1 liter batch reactor at a maximum temperature of 455°C and an average total pressure of 1.3 kPa (run #A051). The pyrolysis oils were recovered in a series of three cooling traps at 0°C, -78°C and -78°C, respectively. Pyrolysis of 147.8g of the RDF sample predried to 80°C produced 44.4% residual solids, 35.1% oils + pitch, 8.1% gas, 9.3% pyrolysis water and 3.1% moisture (wt. %, feedstock as-received basis). On an organic basis, the yields were 23.5% solids, 51.1% oils + pitch, 11.8% pyrolytic water and 13.6% gas. The mass balance closed to 99.7%.

10.2.3 Chemical Analysis Method

The pyrolysis organic phase consisted of a liquid oil phase and a pitch product, which together represented 35.1% by weight of the as-received feedstock. Oil and pitch were studied separatedly in this investigation.

The water content of both samples was determined by the Karl Fisher method (see Table 22).

TABLE 22: % Water Content of Pyrolysis Oil and Pitch (%)

Sample	Water Content (%)
Oil	50.9
Pitch	6.9

Due to its high polarity and high oxygen content, pyrolysis oil was fairly miscible with water.

Recently Evans and Milne (9) applied direct molecular beam, mass spectrometry with multivariate statistical analysis techniques to analyse MSW pyrolysis oils. In this work we report a fractionation scheme and partial analysis of the oil fractions. The analyses were made by means of gas-chromatography (GC) and gas-chromatography coupled to mass spectrometer (GC/MS).

15 g of activated silica-gel (70-230 mesh at 100°C for 3 h) was packed in a glass column 200 mm long x 10 mm i.d.. About 500 mg of the pyrolysis oil was transferred into the column and eluted with various solvents as shown in Table 23. About 400 mg of the pitch sample was preadsorbed on 0.5 g of silica-gel then was transferred into the column packed with 15 g of activated silica-gel. The column was eluted and the results are shown in Table 24. The oil recovery yield was over 90% after fractionation which is considered a good yield. Due to the fact that methanol dissolves a small quantity of silica-gel and difficulties of incomplete removal of ethylacetate, methanol and methanol/formic by evaporation, the yield after fractionation was 106.5% (Table 23).

TABLE 23: Fractionation of Pyrolysis Oil

Fraction #	Eluent*	% yield**
1	Petroleum ether (40-60 bp)	<0.4
2	50% Dichloromethane in petroleum ether	<0.5
3	Dichloromethane	<0.3
4	Ethylacetate	26.4
5	Methanol	74.6
6	10% Formic acid in methanol	4.3
	Total	106.5

* 150 ml of each fraction
** Dry oil basis

TABLE 24: Fractionation of Pyrolysis Pitch

Fraction #	Eluent*	%yield**
1	Petroleum ether	46.6
2	Petroleum ether and dichloromethane (3:1)	9.7
3	Petroleum ether and dichloromethane (1:1)	2.2
4	Petroleum ether and dichloromethane (1:3)	1.8
5	Dichloromethane	1.4
6	Ethylacetate	8.3
7	Methanol	11.4
8	10% Formic acid in methanol	9.6
	Total	91.0

* 150 ml of each fraction
** Dry pitch basis

Various fractions shown in Tables 23 and 24 were analysed by GC and GC/MS. GC and GC/MS operating conditions were as below:

GC conditions: Varian 6000 GC with split mode injection (290°C) and FID detector (300°C). HP-5 capillary column with 50 m x 0.2 mm i.d. with 0.33 µm film thickness was used. GC oven temperature was held 2 min at 50°C then programmed at a rate of 5°C · min^{-1} to 290°C.

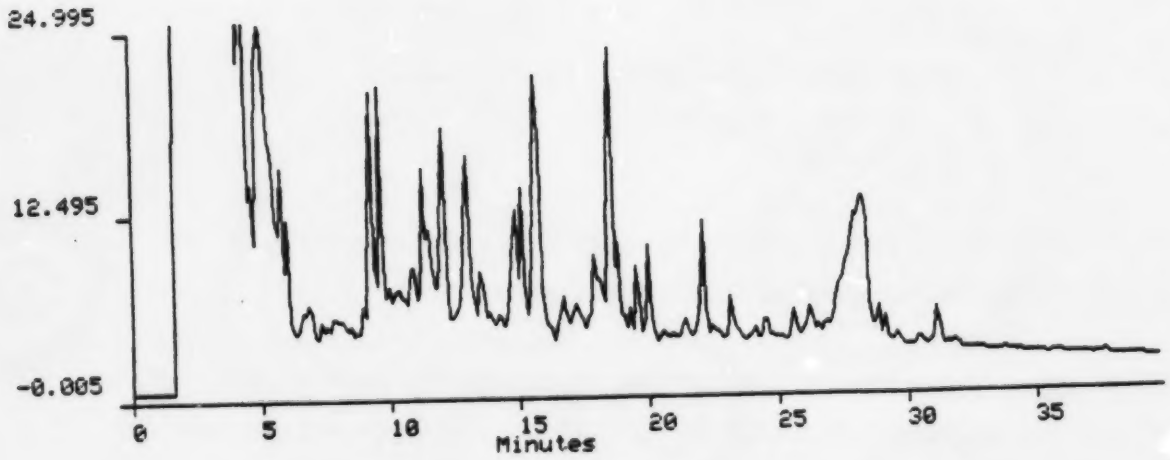
GC/MS conditions: The operating conditions were the followings: HP-5890 gas chromatograph with split injection mode (290°C) and helium carrier gas with about 1 ml · min^{-1} flow rate was used with 30 m x 0.25 mm i.d. capillary column coated with DB5 (J & W) with 0,25 µm film thickness. The GC initial temperature was 50°C for 2 min then

programmed at a rate of 5°C · min^{-1} to 200°C then to 290°C at a rate of 10°C · min^{-1}. The end of the column was introduced directly into the ion source of a HP-5970 series quadrupole mass selective detector. Typical mass spectrometric operating conditions were as follows: transfer line 270°C, ion source 280°C, and 70 eV ionization potential. Data acquisition was done with HP-UX Chemstation software with NBS library data base for peak identification. The mass range m/z = 30-600 Dalton was scanned every 2 seconds.

10.2.4 Pyrolysis Oil Analysis

Figure 16 shows the gas chromatogram of the total pyrolysis oil. Low resolution and broad peaks indicate the high polarity of the oil.

FIGURE 16: Chromatogram of Pyrolysis Oil in Methanol



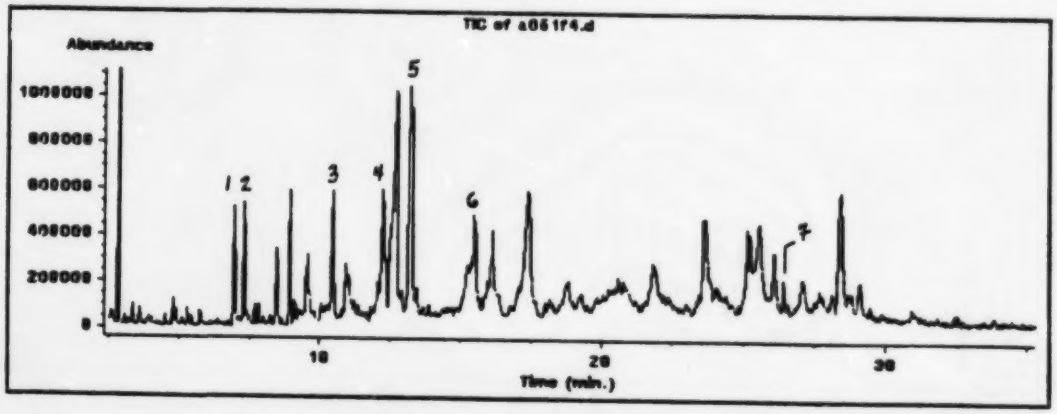
Fractions 1, 2 and 3 (Table 23) did not show any significant peaks in their chromatograms recorded. Figure 17 shows the total ion chromatogram of fraction 4 (Table 25). A few peaks were identified and listed in Table 25.

TABLE 25: Composition of Oil Fraction #4

GC Peak	Tentative Structure
1	2 (3H)-Furanone
2	1,3-Cyclopentanedione
3	2-Cyclopenten-1-one, 2-hydroxy-3-methyl
4	2 (1H)-Pyridinone
5	Maltol
6	Benzoic acid derivative
7	n-Alkyl derivative of benzamide

* See Figure 17

FIGURE 17: TIC Chromatogram of Pyrolysis Oil Fraction #4



Maltol (3-hydroxy-2-methyl-4-pyrone) was identified as the most aboundant component with less ambiguity which has potential economical value.

Due to its high polarity, fraction 5 showed only a large and broad peak which may be a carboxylic acid. The remaining high polar and high molecular weight compounds were eluted in fraction 6 for which we have not made any analysis at this stage.

10.2.5 Pitch Analysis

In contrast to the oil fraction, the pyrolysis pitch showed rather low polarity and contained partially aliphatic and aromatic compounds. GC and GC/MS analysis results of fractions 1 to 5 are shown respectively in Figures 18 to 22. Figure 18 shows the distribution of homologous series of n-alkanes and n-alkenes (C_{11} to C_{47}) which contributed for about 46.6% of the total dry pitch.

FIGURE 18: Chromatogram of Pyrolysis Pitch Fraction # 1

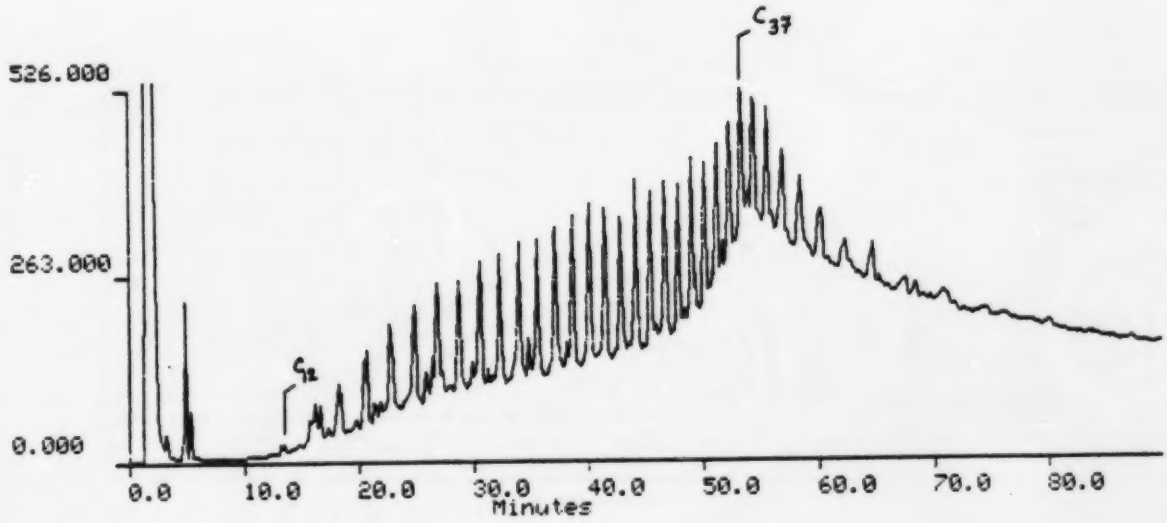


Table 26 shows a list of compounds identified in fraction 2 which are mainly benzene derivatives.

Table 26: Composition of Pitch Fraction #2

GC Peak #	Tentative Structure
1	2 or 4-methylbiphenyl
2	1,1-Bis (1,2-ethanediyl) benzene
3	1,1-Bis (1,3-propanediyl) benzene
4	1,1-(Alkyl derivative) benzene
5	1-Methyl-2-(2-phenylethenyl) benzene
6	1,1- Bis(1,4-butanediyl) benzene
7	1,1-(Alkylderivative) benzene
8	9,10-Dimethylphenanthrene
9	1,1-Bis (3-methyl-1-propene-1,3-diyl) benzene
10	1,4-Dihydro-1,4-ethenoanthracene
11	5-Methyl-2-phenyl-1H-indole

* See Figure 19

FIGURE 19: TIC Chromatogram of Pyrolysis Pitch Fraction # 2

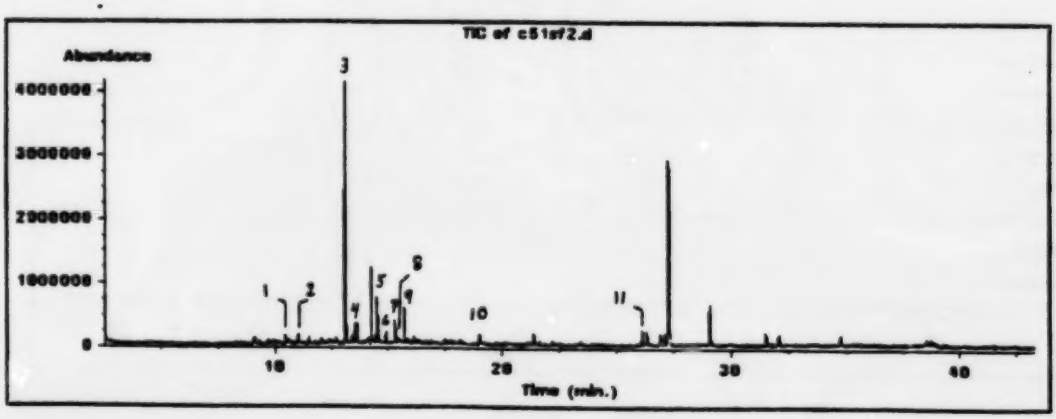


Table 27 shows the major compounds identified in fraction 3. Whether esters in Table 27 are produced by pyrolysis or were present in the initial feedstock is unknown. No further investigation was made at this stage.

Table 27: Composition of Pitch Fraction #3

GC Peak #	Tentative Structure
1	Hexadecanoic acid methylester
2	Octadecanoic acid methylester
3	Similar to 2
4	16- Methyl heptadecanoic acid methyl ester

* See Figure 20

FIGURE 20: TIC Chromatogram of Pyrolysis Pitch Fraction # 3

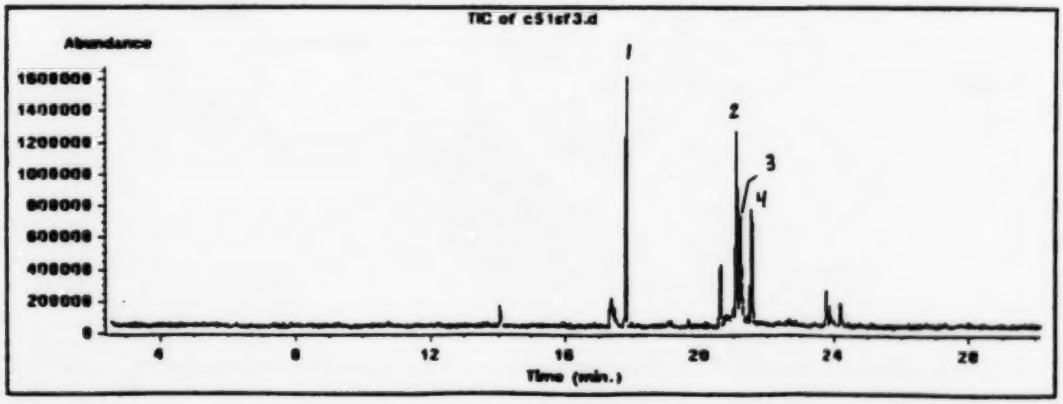


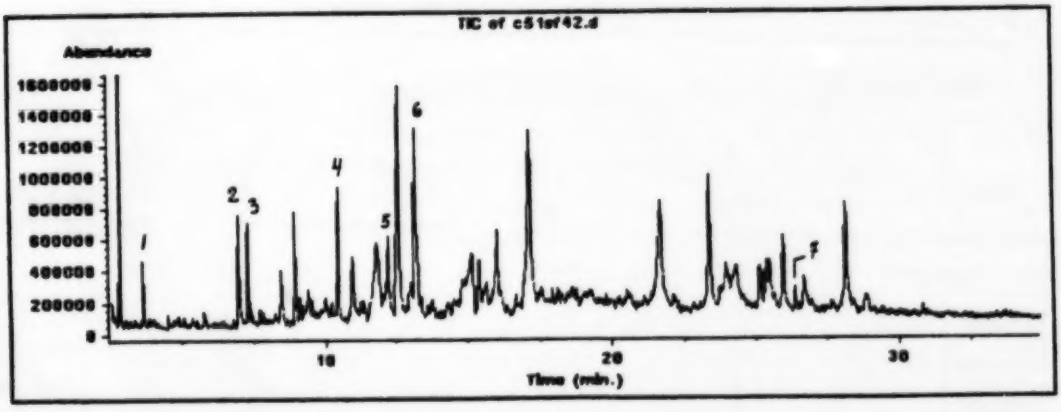
Table 28 shows the compounds identified in fraction 4.

Table 28: Composition of Pitch Fraction #4

GC Peak #	Tentative Structure
1	Toluene
2	2(3H)-Furanone
3	1,3-Cyclopentanedione
4	3-Methyl-1,2-cyclopentanedione
5	Furancarboxylic acid methyl ester
6	Maltol
7	3-Methyl-N, N-diethylbenzamide

* See Figure 21

FIGURE 21: TIC Chromatogram of Pyrolysis Pitch Fraction # 4



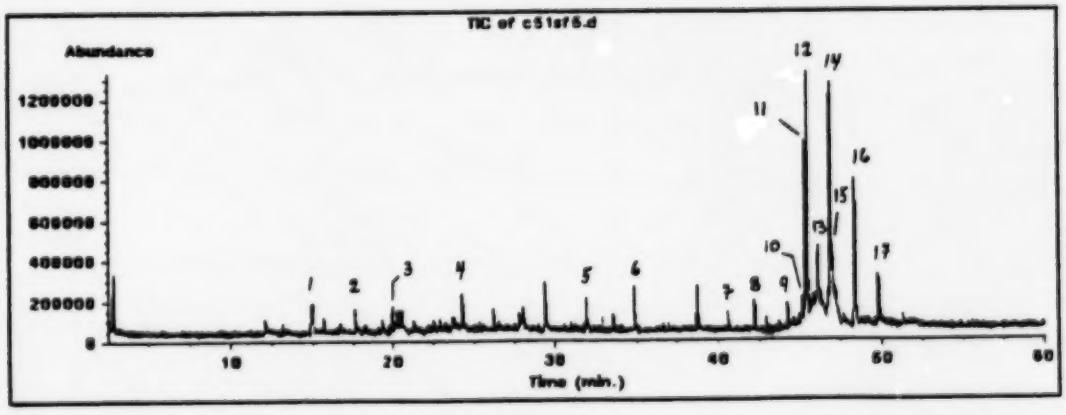
Fraction 5 contained simple phenols and several phthalic and terephthalic acids ester derivatives, the typical plasticides.

Table 29: Composition of Pitch Fraction #5

GC Peak #	Tentative Structure
1	3,5-Dimethylphenol
2	2-Ethyl-6-methylphenol
3	2,3-Dihydro-1H-inden-5-ol
4	1,4-Benzenedicarboxylic acid dimethyl ester
5	1,4-Benzenedicarboxylic acid ethylmethyl ester
6	1,2-Benzenidicarboxylic acid butyl 2-methylpropyl ester
7	1,2-Benzenidicarboxylic acid butyl decyl ester
8	Benzyl butyl phthalate
9	1,2-Benzenedicarboxylic acid bis (2-methoxyethyl) ester
10	1,2-Benzenedicarboxylic acid mono (2-ethyl hexyl) ester
11	1,2-Benzenedicarboxylic acid diheptyl ester
12	1,2-Benzenedicarboxylic acid diisooctyl ester
13-17	1,2-Benzenedicarboxylic acid alkyl esters

* See Figure 22

FIGURE 22: TIC Chromatogram of Pyrolysis Pitch Fraction # 5



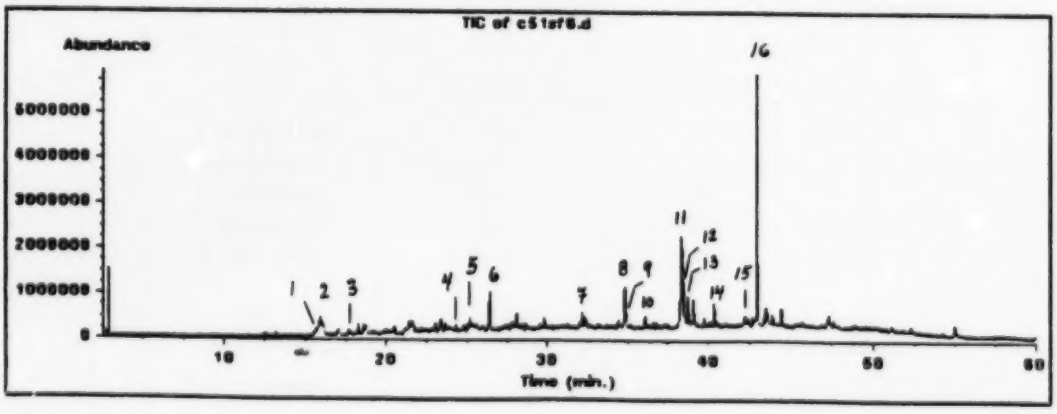
Fractions 6, 7 and 8 in Table 24 represented about 29% of the dry pitch. The total ion chromatograms of fractions 6 and 7 are shown in Figures 23 and 24, respectively.

Table 30: Composition of Pitch Fraction #6

GC Peak #	
1	2-Methoxy-4-methylphenol
2	1,2-Benzenediol
3	3-Methyl-1,2-benzenediol
4	Alkylester of 1,4-benzenedicarboxylic acid
5	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone
6	N-(1,1-Dimethylethy)-4-methylbenzamide
7	N-dodecylbenzamide
8	Hexadecanoic acid
9	Alkylester of 1,2-Benzenedicarboxylic acid
10	4-(1,5-dimethyl-3-oxohexyl)-1-cyclohexene-1-carboxylic acid
11	9-Octadecenoic acid
12	14-Pentadecenoic acid
13	Octadecnoic acid
14	Hexadecanamide
15	9-Octadecenamide
16	Hexanedioic acid dioctyl ester

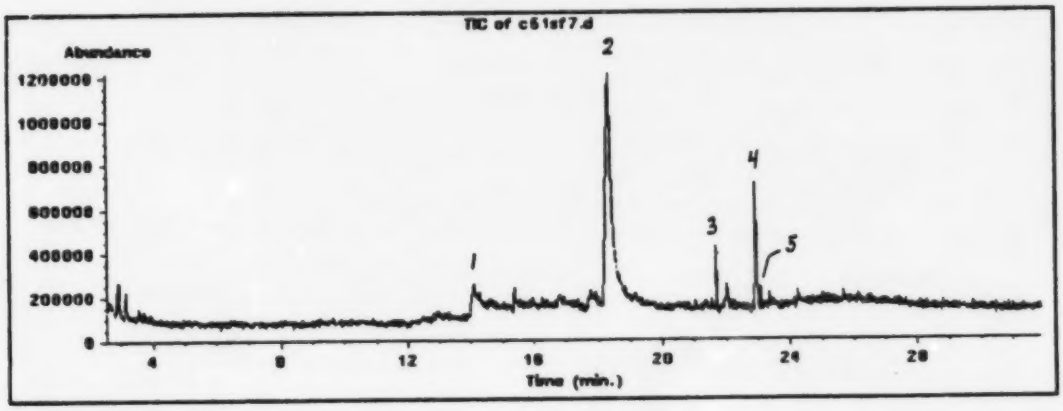
* See Figure 23

FIGURE 23: TIC Chromatogram of Pyrolysis Pitch Fraction # 6



Fraction 6 mainly contained polar compounds like diphenols and carboxylic acids. Even higher polar compounds were eluted in fractions 7 and 8 which we were unable to characterize further at this stage. However, we believe those are composed of low molecular weight polar compounds, mainly carboxylic acids and their derivatives (see Figure 24).

FIGURE 24: TIC Chromatogram of Pyrolysis Pitch Fraction # 7



10.2.6 Sugar Analysis

Both the pyrolysis oil and pitch samples were hydrolyzed prior to their sugar analysis. The hydrolyzates were then derivatized to their trimethylsilyl derivatives (10). Qualitative and quantitative analysis were made on a capillary gas chromatograph. GC operating conditions were as below.

- Varian 3700 gas chromatograph with "on-column" mode injector (programmed at rate of 180°C min^{-1} from 40°C to 290°C) and FID detector (300°C). DB-1 capillary column with 30 m x 0.2 mm i.d. and 0.25 µm film thickness was used. GC oven temperature was held 4 min at 140°C then programmed at a rate of 2°C · min^{-1} to 290°C.

Table 31 shows the major sugar content of both the pyrolysis oil and pitch. A significant quantity of sugars (17%) were found in the pyrolysis oil whereas pitch showed only about 1%. In both products glucose was the most aboundant sugar and contributed about 67% of the total sugars.

Table 31: Sugar Content of Pyrolysis Oil and Pitch

Sugar	wt%	
	Pyrolysis Oil	Pyrolysis Pitch
Arabinose	2.2	0.2
Xylose	0.8	0.1
Mannose	2.4	0.1
Galactose	0.3	0.1
Glucose	11.6	0.6
Total	17.3	1.1

* Dry basis

10.2.7 Pyrolysis Gas Analysis

The non condensable gas composition is given in Table 32.

Table 32: Gas Composition (vol. %)

CH_4	7.9
CO	24.4
CO_2	57.4
C_2H_4	1.6
C_3H_6	0.9
C_3H_8	5.3
Others	0.6
Molecular weight Gross	37.4
calorific value ($cal \cdot g^{-1}$)	2190

A more detailed analysis of the "other components" of the gas phase was conducted using a GC/MS apparatus. The objective was to detect any contaminants such as chlorinated hydrocarbons. The GC temperature was maintained at 35°C for 2 min then programmed at rate of $5°C \cdot min^{-1}$ to 100°C. The injection temperature was 100°C. From their abundance in the total ion chromatogram the gases were classified into two groups:

- Major compounds including chloroethane, chloromethane, 2-methylfuran and benzene.

- Minor compounds including vinylchloride, diethylether, dichloromethane, chloroform, toluene and dimethyldisulfide.

10.2.8 Carbonaceous Solid Residue Analysis

The proximate analysis of the solid residues gave 11.6% volatile matters, 62.0% ash and 26.4% fixed carbon. The hygroscopic moisture in the sample was 1.4%.

10.3 Comments on Pyrolysis of MSW

Pyrolysis oil and pitch account for more than 50% of the products from MSW on an organic basis. Pyrolysis oil was mainly oxygenated in nature and is believed to have a low molecular weight distribution range. Significant quantity of maltol (~ 1%) was positively identified which is a food aroma. In addition we found about 17% sugar, mainly glucose. Complete toxicity measurement of the oil has not been made. However we have not identified at this point any priority pollutants including chlorinated and nonchlorinated volatile hydrocarbons, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in the oil phase. Only trace amounts of chlorinated volatiles were observed in the gas phase. The oil may have a low concentration of phenolic compounds which could be easily separated if it is required.

Pyrolysis pitch is particularly attractive since it can be fractionated into interesting classes of compounds such as aliphatic hydrocarbons, benzene derivatives, carboxylic acid esters, phenolic compounds and phthalate esters. These contributed for about 70-80% of the total pitch. Aliphatic hydrocarbons can be used as wax, phthalate esters can be recycled in the polymer industry as plasticizers and carboxylic esters can be returned in the detergent manufacture.

11.0 CONCLUSIONS

The PDU was operated during sufficient lengths of time to establish good mass and energy balances. Condensation with quenchers at the primary and secondary condensing units (PCU and SCU) proved successful. It appears possible to adjust the operation conditions, such as the temperature of the PCU and the internal pressure of the system, in order to obtain oil with a low water content. Some problems were encountered with the solid feeding system of the multiple hearth reactor. However we consider these are minor difficulties that can be solved easily with an improved mechanical design.

The heat requirement for the pyrolysis of wood residue is around 400 $kJ \cdot kg^{-1}$ (wood feedstock basis). Also in our relatively small scale PDU, heat losses to the atmosphere are quite important since they represent roughly 1/3 to 1/2 of the total electric power required by the reactor. The heat transfer coefficient for the outer shell of the reactor with the ambient atmosphere was estimated between 5.6 and 7.3 $W \cdot m^{-2} \cdot C^{-1}$. Also the ratio of the effective pumping power for the pyrolytic vapors and gas over the total pumping power is in the 10% range. The heat transfer coefficients mesured in the quencher at the PCU were between 121 and 142 $W \cdot m^{-2} \cdot C^{-1}$. The heat required for the cooling of the charcoal was around 465 $kJ \cdot kg^{-1}$ charcoal.

A preliminary evaluation showed the feasibility of a 4 000 $tg \cdot h^{-1}$ plant for the treatment of wood chips. The process requires the drying of the wood chips to 10% humidity content prior to the pyrolysis itself. An economical estimation revealed the profitability of the process if the solid charcoal is sold as active carbon. However the addition of a tipping fee of $30/tonne makes the process even more attractive.

Separation of the chemicals from the oil was performed in a reproductive way with a liquid chromatography (LC) technique at the 100 g scale. Valuable fine chemicals such as vanillin were identified and separated. More work need to be done to improve or replace the LC technique used in order to make chemicals purification enonomically profitable.

Finally laboratory scale pyrolysis tests were performed on MSW. Many chemcials such as maltol and glucose were identified in the oil and pitch fractions. No priority pollutants including chlorinated and non chlorinated volatile hydrocarbons, polycyclic aromatic hydrocarbons and polychlorinated biphenyls have been identified in the oil so far.

RECOMMENDATIONS

Following this study some recommendations can be made. These may prove useful for future work:

1- More intensive work will need to be done on the chemical separation and upgrading techniques of the oil components. HPLC and membrane separation could be alternate promising techniques.

2- Upgrading of the wood pyrolysis charcoal to activated carbon positively influences the process profitability. We recommend to undertake a laboratory study on the activation of wood pyrolysis charcoal. Such study could help in establishing the quality of the activated carbon and evaluating its market value.

3- Considering the growing problem of Municipal Solid Wastes accumulation, it would be quite relevant to launch a research and development program to experiment vacuum pyrolysis at the P.D.U. level.

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APPENDICE I

Equipment Specification for the 4 000 kg h^{-1} Pyrolysis Plant

EQUIPEMENT	CODE	DESCRIPTION
Rotary Dryer	RD-1	Heat source:Wood,Gas,oil Capacity: 8000 kg · h^{-1} Heat requirement: 3700kWh Power requirement: 125 HP
Vacuum Feeder	VF1	Capacity: 4 000 kg · h^{-1} Type: internal screw piston
Pyrolysis Reactor	PR-1	Type: Multiple Hearth furnace Capacity: 1.33 tph Material: shell SS316 plate SS304 Diameter: 2.25 m Height: 10 m Numer of hearths: 20 Heating: Electric radiant Glowbars Electric Power: 433 kW
	PR-2	same as PR-1
	PR-3	same as PR-1

Condenser	LC-1	Type: Quench Tower Material: SS 304 Diameter: 2.3 m Height: 9 m Temperature: liquid 30→40°C, Vapor 335→35°C Liquid capacity 500 GPM
	LC-2	Type: same as LC-1 Temperature: liquid 20→23°C Vapor 35→20°C Liquid capacity capacity:1100GPM

Heat exchanger	HE-1	Type: Water jacket Area: 0,75 m^2 Cooling Water: 25→50°C, 4GPM Charcoal: 435→150°C 320 kg · h^{-1}
	HE-2	Same as HE-1
	HE-3	Same as HE-1
	HE-4	Type: Shell and tubes Area: 135m^2 Cooling water: 20→23°C, 930 GPM From HE-5 To HE-1.2.3. Process liquid: oil, 40→30°C, 500GPM Material: shell: CS tubes: SS 304
	HE-5	Type: Shell and Tubes Area: 175m^2 Cooling water: 17→20°C, 930 GPM to HE-4 Process liquid: water + oil, 23→20°C,1100 GPM

Circulation pump	CP-1	Type: centrifugal Material: SS 304 Capacity: 500 GPM Power: 25 HP
	CP-2	Type: centrifugal Material: SS 304 Capacity: 1100 GPM Power: 40 HP
	CP-3	Type: centrifugal Material: SS 304 Capacity: 6.25 GPM Power: 0,3 HP
	CP-4	Type: centrifugal Material: CS Capacity: 30 GPM Power: < 5 HP
Centrifuge	BC-1	Continuous operation Capacity: 5380 kg · h^{-1} Material : SS 316

Vacuum pump	VP-1	Two stage system 1- Blower 2- Liquid ring pump Operation:20->80 mmHg Capacity: 4500 cfm
Storage tank	ST-1	Type: flat top + bottom Capacity: 10000 USGal Material: SS 304
	ST-2	same as ST-1
	ST-3	Capacity: 500 USGal Material: SS 304
Transfer bin	TB-1	Dimensions: diameter: 1.25m height: 1.5m Material : CS
	TB-2	same as TB-1

Separator	CS-1	Type: Drop-out box
	CS-2	Type: Cyclone Capacity: 32000 cfm Material: CS
	CS-3	Type: Cyclone Capacity: 4500 cfm Material: SS 304
Conveyer	C-1	Type: Belt Lenght: 25m, Width: 36cm
	C-2	Type: Belt Lenght: 75m width: 36cm
	C-3	Type: Belt Lenght: 100m Width: 36cm
	C-4	Type: Belt Lenght: 25m Width: 36cm

Screw	S-1	Type:constant pitch diameter: 23cm Lenght: 20m Material: SS 304
	S-2	same as S-1
	S-3	Same as S-1
	S-4	Type: variable pitch diameter: 10cm Material: SS 316
	S-5	Same as S-4
	S-6	Same as S-4
Biomass mill	BM-1	Type: Hammer mill Capacity: 400 kg · h^{-1}
Vibratory Screen	VS-1	Capacity: 500 kg · h^{-1}